**Energetic Cost for Being “Redox-Site-Rich” in Pseudocapacitive Energy Storage with
Nickel – Aluminum Layered Double Hydroxide Materials**

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Abstract

As an alternative to rechargeable batteries, pseudocapacitors feature high power density, fast charge – discharge kinetics and long cycling stability for energy storage. Compositional modification by redox site enrichment is an effective strategy to increase the energy density and enhance the Faradaic reactions of pseudocapacitive materials. Transition metal layered double hydroxides (TM-LDHs) feature a layered structure and modifiable transition metal content for pseudocapacitive energy storage. In an earlier report, we demonstrated that for NiAl-LDH materials increase of Ni/Al ratio leads to expanded van der Waals (vdW) gap enabling fast charge–discharge kinetics, degraded crystallinity, and retention of 2D layered structure featuring high cycling stability. Here, coupling near-room temperature acid solution calorimetry, *in situ* X-ray diffraction (XRD), and *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), we find that as the Ni/Al ratio increases, both as-made (hydrated) and dehydrated NiAl-LDH samples tend to be less stable evidenced by experimentally measured enthalpies of formation. Moreover, the higher specific capacity of NiAl-LDH-3 (2128 F/g at 1 A/g) is enabled by effective hydration which energetically stabilizes the near-surface Ni redox sites, solvates intercalated carbonate ions, and fills the expanded vdW gap (interlayer space). In other words, for NiAl-LDH, water – LDH interactions pay for the “energetic cost” of being “redox site rich”. Thus, from a thermodynamic perspective this work points out a strategy to introduce and energetically stabilize the redox sites in TM-LDHs through interfacial engineering for pseudocapacitive energy storage performance enhancement, in which other species, including solid state guests may be introduced into the interlayer gallery.

Introduction

Electrochemical energy storage devices, primarily batteries and capacitors, are playing critical roles in the ongoing modification of our energy infrastructure ^[1–6]. Rechargeable battery materials rely on phase transitions and/or solid-state reactions during the charge–discharge processes, while capacitive energy storage mechanisms take advantage of the electrostatic charge storage at or near the surface of the electrode materials ^[7–10]. Compared with the “endurance athletes” – rechargeable batteries that have high energy density, the advantages of electrochemical capacitors include high power density, long cycle life, and rapid charge – discharge. These properties enable high performance “sprinter” energy storage devices for short-term charge storage, regenerative braking, and burst-mode delivery of energy ^[11–15].

Depending on the working mechanisms, electrochemical capacitors are typically categorized as (1) electrical double-layer capacitors (EDLCs or supercapacitor) and (2) pseudocapacitors ^[11–15]. EDLCs rely on the formation of an ionic double layer at the electrode – electrolyte interfaces for electrical energy storage. Despite their low cost and wide availability, the carbon-based EDLCs suffer from low energy density because of the limitation of surface area and effective interfaces ^[16–20]. In this regard, pseudocapacitors feature substantially increased energy density accompanied with high power density, rapid charge transfer kinetics, and cycle stability ^[21–26]. Fundamentally, pseudocapacitive materials store charge at or near their surfaces by reversible redox reactions based on Faradaic charge transfer, in which the *concentration of redox sites* are a governing factor of the specific capacitance ^[22,27,28]. Thus, understanding the impacts of redox site concentration on the phase stability, structure, and storage of pseudocapacitive materials, such as transition metal oxides ^[22,25,26], hydroxides ^[12,13], and sulfides ^[29,30] along with conductive polymers ^[31], is essential for further materials discovery, rational design, and optimization.

This paper elucidates the energetics – structure – performance relationships of transition metal layered double hydroxides (TM-LDHs) as the redox site concentration is tuned. TM-LDHs possess positively charged brucite-like metal hydroxide layers constructed by M^{2+} and M^{3+} transition metal octahedra [32]. Introduction of trivalent cations M^{3+} into the $M^{2+}(\text{OH})_2$ layer leads to layer-possessed positive charges (redox sites) and simultaneous intercalation of charge-balancing anions (A^{n-}) confined within the interlayer space, which is also filled by neutrally charged guest species, such as water molecules [12,33]. The open 2-dimensional structure of TM-LDHs enables highly efficient Faradic redox reactions at the near-surface transition metal sites with fast kinetics. In an earlier study of NiAl-LDH with CO_3^{2-} as the charge-balancing anions, we demonstrate that an increase in Ni/Al ratio from 2 to 4 leads to increased Ni redox site concentration, expanded van der Waals (vdW) gap resulting in faster charge transport kinetics, and degraded near-surface crystallinity [21]. We also find that the pseudocapacitive charge storage capacity is *not* positively correlated to the Ni/Al ratio. Additionally, high near-surface crystallinity is crucial to ensure high pseudocapacitive capacitance [21,22,25]. However, the thermodynamic mechanisms for the complex interplays among Ni redox site concentration, near-surface crystallinity, and intercalation chemistry of NiAl-LDHs have not been clearly and quantitatively identified from microscopic and macroscopic perspectives.

Here, we report a systematic study that elucidates the impacts of Ni content on the energetic stability and thermodynamics – structure – performance relationship of NiAl-LDH by integrating two powerful *in situ* techniques, *in situ* X-ray diffraction (XRD) and *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), with the unique calorimetric methods in our lab, including near-room temperature acid solution calorimetry and water adsorption calorimetry. The obtained results suggest that Ni enrichment leads to decreased energetic, thermal, structural,

and morphological stability for both as-made (hydrated) and dehydrated NiAl-LDHs. Further, we demonstrate that the intercalated (2D-confined) water molecules substantially neutralize the significant metastability introduced by Ni redox site enrichment, and the optimized specific capacitance is the result of the subtle balance between the energetic stability of LDH layers and water – layer guest – host interactions. This work also highlights the power of integrating *in situ* structural, spectroscopy and thermodynamic techniques to unravel fundamental mechanisms underlying the properties and behavior of energy storage materials at application conditions.

Experimental Methods

Materials Synthesis

All chemicals used were purchased from Sigma-Aldrich with ACS reagent grade. NiAl-LDH samples were prepared hydrothermally using a Teflon-lined autoclave. Each sample was denoted as NiAl-LDH-*n* according to the Ni/Al ratio (*n*). Specifically, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ($\text{Ni}/\text{Al} = n$, and $\text{Ni} + \text{Al} = 1.875 \text{ mmol}$) were dissolved in 25 ml nanopure water ($18.2 \text{ M}\Omega \cdot \text{cm}$). For NiAl-LDH-2, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were 1.25 and 0.625 mmol, respectively; for NiAl-LDH-3, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were 1.460 and 0.456 mmol, respectively; for NiAl-LDH-4 and NiAl-LDH-2, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were 1.25 and 0.365 mmol, respectively. In addition, the precipitant used was hexamethylenetetramine (HMT, 2.20 mmol) for NiAl-LDH-2, and urea (4.13 mmol) was applied to precipitate NiAl-LDH-3 and 4. In each synthesis, the mixture was introduced into a 50 mL Teflon-lined autoclave for the hydrothermal reaction at 180 °C for 72 hours. The precipitates were filtered and washed with nanopure water ($18.2 \text{ M}\Omega \cdot \text{cm}$) followed by drying under vacuum at room temperature ^[21].

Ex Situ Powder X-ray Diffraction (XRD), Compositional and Thermal Analyses

For phase identification, room temperature *ex situ* powder X-ray diffraction (XRD) patterns of the synthesized NiAl-LDH samples were collected with a Rigaku Miniflex 600 diffractometer (40 kV, 15 mA with Cu $K\alpha$ radiation, $\lambda = 0.15418$ nm). Data were recorded between 5 and 80° at 1 °/min. Compositional and thermal analyses were performed in our earlier study [21]. The chemical compositions of all samples were characterized using inductively coupled plasma-mass spectrometry (ICP-MS, Agilent 770). The TG-DSC-MS thermal analyses were carried out on a Netzsch Instrument STA 449 F3 Jupiter coupled to a QMS 403 D Aëolos quadrupole mass spectrometer in our earlier study emphasizing energy storage performance. In each measurement, about 20 mg sample was analyzed in a platinum from 30 to 1000 °C at 10 °C/min under N₂ flow (20 cc/min). Evolved gases of TG-DSC experiments were identified simultaneously by the coupled MS. Data monitored include $m/z = 18$ (H₂O) and 44 (CO₂). All the *ex situ* XRD, ICP-MS, and TG-DSC-MS data have been reported in our earlier study on the same set of NiAl-LDH samples [21].

N₂ Adsorption and Desorption Full Isotherm Analysis

The Brunauer-Emmett-Teller (BET) and Barrett, Joyner, and Halenda (BJH) surface area and pore size distribution analyses were carried out using N₂ adsorption and desorption full isotherm analysis at 77 K on a Micromeritics 3Flex gas adsorption analyzer. Before each measurement, the sample was degassed *in situ* at the analysis port at 250 °C for 2 hours.

Electron Microscopy (EM)

We examined the sample morphology using scanning electron microscopy (SEM, Quanta 200F), transmission electron microscopy (TEM, FEI Tecnai T20 with a LaB₆ cathode at 200 kV) in Franceschi Microscopy and Imaging Center at Washington State University and high-resolution

transmission electron microscopy (HRTEM, FEI Titan 80-300 TM with monochromator, image aberration corrector, and a PHENIX energy dispersive X-ray spectrometer detector) at Los Alamos National Laboratory. *ImageJ* (NIH) was employed for micrograph analysis ^[34]. The SEM specimen was prepared by loading the sample on carbon tape, which was placed on an aluminum stub. The specimen for TEM and HRTEM analyses were prepared by dispersing a small amount of sample powder in ethanol using ultrasonication. Subsequently, several drops of suspension were introduced and dried on 200-mesh carbon-coated nickel grid (TEM) and a 200-mesh carbon-coated copper grid (HRTEM).

In Situ X-ray Diffraction (in situ XRD)

The structural evolution of all NiAl-LDH samples as temperature increases from room temperature to 600 °C was monitored by *in situ* powder X-ray diffraction (*in situ* XRD). The data were obtained using a Rigaku Smartlab X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) coupled with a platinum strip heater operated at a scan rate of 4 °/min in the 2θ range of 5–80° with a heating rate of 10 °C/min under 30 ml/min of helium with a hold time of 5 min prior to each scan. d -spacing was calculated using Bragg's law. The lattice parameters and unit cell volume of each sample were calculated. PDF database references were used to identify the phases of hydrotalcite (naturally occurring $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$), PDF-Card No. 00-014-0191, NiO, PDF-Card No. 01-073-1519, and Al_2O_3 , PDF-Card No. 01-073-5928.

In Situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy (in situ DRIFTS)

In situ diffuse reflectance infrared Fourier transform spectroscopy (*in situ* DRIFTS) analysis was carried out in a high-temperature cell (Spectra-Tech[®]) equipped with ZnSe windows (IR transparent). Prior to each analysis, the sample was finely ground and placed in a ceramic

crucible. The spectra were recorded from room temperature to 500 °C under helium (He) flow (50 mL/min). The background spectra were collected under the same condition. We were not able to reach 600 °C as we did in the *in situ* XRD experiments due to the instrument limit.

Figure 1. Illustrated structures (a, b, c) and morphologies of NiAl-LDH samples revealed by scanning electron microscopy (SEM, d, e, f), transmission electron microscopy (TEM, g, h, i), and high-resolution transmission electron microscopy (HRTEM, j, k, l), NiAl-LDH-2 (gray), NiAl-LDH-3 (red), and NiAl-LDH-4 (navy).

Near-Room Temperature Acid Solution Calorimetry

Near-room temperature acid solution calorimetry (HCl, 5 mol/L, Sigma Aldrich) using a Setaram C80 microcalorimeter was employed to measure the enthalpies of dissolution to derive the NiAl-LDH formation enthalpies. In a typical measurement, a loose, hand-pressed sample pellet (~4 mg) was dropped into the HCl solution (10 mL) kept at 40 °C. The slightly elevated temperature aided rapid dissolution of NiAl-LDH pellet, which led to a calorimetric peak. Similar strategy was also applied in an earlier study on porous silica using hydrofluoric acid (HF) solution calorimetry at 50 °C, in which the temperature effects were negligible [35]. The completion of sample dissolution was confirmed by the return to a flat baseline. Integration of the area under each calorimetric peak returned the heat of dissolution (kJ) for each pellet. At least 4 successful measurements were performed on each sample to ensure reproducibility. The error bars were calculated as two standard deviations of the mean. KCl (NIST) dissolution was used to calibrate the microcalorimeter.

Results and Discussion

Morphology, Structure, and Surface Analyses

The illustrated structures and electron microscopy images are presented in **Figure 1**. As seen from the SEM and TEM images, NiAl-LDH-2 possesses hexagonal platelet nanosheet morphology, while the shape of NiAl-LDH-3 and 4 platelet nanosheets appear to lack well-defined geometry. Investigated by HRTEM, NiAl-LDH-4 appears nearly amorphous at atomic scales in the interplanar direction with many jagged grain boundary defects near the layer-edges. By contrast, NiAl-LDH-2 and NiAl-LDH-3 appear to have better near-surface crystallinity than NiAl-LDH-4 with smooth rounded layer-edges. As the Ni/Al ratio increases, the particle size decreases

from ~250 nm for NiAl-LDH-2 to ~80 nm for NiAl-LDH-4. The N₂ adsorption and desorption full isotherm analysis data are plotted in **Figure 2** and summarized in **Table S1**. The specific surface area increases as the Ni/Al ratio increases. Specifically, the BET specific areas are 47.5, 77.0 and 152.1 m²/g for NiAl-LDH-2, 3 and 4, respectively. This trend is consistent with the particle size decrease observed in the electron microscopy analyses. In addition, in BJH pore size analysis, NiAl-LDH-3 presents the largest pore size of 22.3 nm, while NiAl-LDH-4 has the smallest mesoscale porosity of 8.0 nm. In general, Ni enrichment leads to decreased particle size, degraded morphology, increased surface area, and decreased pore size.

Figure 2. (a) Nitrogen adsorption and desorption full isotherms and pore size distribution of (b) NiAl-LDH-2, (c) NiAl-LDH-3, and (d) NiAl-LDH-4.

Figure 3. *In Situ* X-ray diffraction (XRD) patterns of all samples as a function of temperature from 25 to 600 °C at 10 °C/min under helium flow of 30 ml/min with a hold time of 5 minutes at each temperature prior to measurement. Data were collected from 5 to 80°. **(a)** NiAl-LDH-2, **(b)** NiAl-LDH-3, and **(c)** NiAl-LDH-4. **(d)** Lattice parameters of all NiAl-LDH samples as a function of temperature.

Structural Evolutions

In situ XRD patterns for NiAl-LDH samples are presented in **Figure 3a, b** and **c**. All samples exhibit hydroxide-like structures representative of metal hydroxide layered structures. Generally, before eventual degradation as the temperature increases the representative XRD peaks of each NiAl-LDH broaden and shift to higher 2θ s. Phase transition due to degradation of the brucite-like metal hydroxide layered structure was observed at above 300 °C for NiAl-LDH-2 and 3, and 250 °C for NiAl-LDH-4. At temperatures higher than 400 °C, each sample decomposes to a mixed phase of NiO and Al₂O₃, shown in **Figure S2**. Lattice parameters of the NiAl-LDHs in hexagonal close packing found from representative peaks of (003) and (110) are presented as a function of temperature in **Figure 3d**. The a lattice parameter, which represents the cell dimension parallel to the brucite-like layer, does not change appreciably throughout the temperature range investigated. Seen in our previous work and repeated here, the c lattice parameter (related to the

d -spacing by the equation $c = 3 \times d_{003}$) at 25 °C, which represents the cell dimension in the interlayer direction, increases with Ni content [21]. As Ni content increases and Al content decreases, the total positive charge of the metal hydroxide layer lessens; proportionately, interlayer charge balancing anions decrease limiting electrostatic interactions [21]. As temperature increases, the c lattice parameter of each sample decreases. The c lattice parameters exhibit 3 ~ 4 Å relatively abrupt decrease from 200 to 250 °C for NiAl-LDH-2, and from 150 to 200 °C for NiAl-LDH-3. Such stepwise decrease is indicative of the loss of one layer of intercalated water (dehydration), since interlayer-confined water molecules are ~2.5 Å in size [36]. Interestingly, NiAl-LDH-3 seemingly expands its interlayer distance from 250 to 300 °C. We attribute this to be normal lattice thermal expansion or an artifact from the growing disorder in stacking, while carbonate deintercalates and subsequent structural degradation observed from the wide distribution of the (003) peak at 300 °C (see **Figure 3b**). The c parameter of NiAl-LDH-4 features a much more gradual decrease for ~4 Å spanning from 25 to 200 °C, presumably due to more chaotic stacking (seen in SEM and/or TEM) leading to varied interlayer environments. As Ni content increases interlayer dehydration occurs at lower temperatures. In summary, the *in situ* XRD results strongly highlights (1) the loss of interlayer space after dehydration of intercalated water, and (2) phase transition to oxide phases at temperature above 400 °C, which is accompanied by release of CO₂ (see the TG-DSC-MS data plotted in **Figure S1**) [21].

Interfacial Phenomena

The *in situ* DRIFTS spectra suggest all NiAl-LDH samples share three vibrational features (see **Figure 4**), including (1) a broad absorption spanning from 4000 to 2500 cm⁻¹ owing to the O–H stretching vibration of hydroxyl groups from the brucite-like layers and intercalated water molecules; (2) three overlapped peaks between 2000 and 650 cm⁻¹ due to interlayer-confined H₂O

and carbonate species, and surface OH groups, specifically, one at $\sim 1650\text{ cm}^{-1}$ (bending vibration of adsorbed water), and two between 1370 and 1000 cm^{-1} (asymmetric stretching of interlayer carbonate species); (3) several relatively weak absorption peaks between 1000 and 650 cm^{-1} belonging to lattice vibration of the metal – oxygen bonds within the NiAl-LDH layer.

Figure 4. *In Situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) spectra of each sample as a function of temperature from 50 to 500 °C under helium flow of 50 ml/min, (a) NiAl-LDH-2, (b) NiAl-LDH-3 and (c) NiAl-LDH-4.

Both *in situ* DRIFTS and TG-DSC-MS results strongly suggest a *two-stage mechanism* for thermal degradation of NiAl-LDH. Specifically, in **Stage I** interlayer dehydration (from 25 to $\sim 200\text{ }^{\circ}\text{C}$), starting from $\sim 150\text{ }^{\circ}\text{C}$ a sharp peak at 3680 cm^{-1} appears, which is assigned to $\nu(\text{OH})$ of isolated surface hydroxyl groups of LDH [37]. Interestingly, although this peak is clearly well-resolved for NiAl-LDH-2 and 3, it appears to be very broad and nearly undetectable during **Stage I** dehydration of NiAl-LDH-4. Dehydration in **Stage I** leads to removal of intercalated water molecules reducing the hydrogen bonding among interlayer adsorbed/confined species. As

temperature increases, the low wavenumber peaks of NiAl-LDH-2 become better resolved, splitting into three sharp peaks centered at 1600, 1370, and 1130 cm^{-1} . For NiAl-LDH-3 and 4, shift from 1650 to 1600 cm^{-1} and from 1420 to 1370 cm^{-1} were observed. The signal at $\sim 1600 \text{ cm}^{-1}$ is attributed to the bending mode of exposed surface OH groups from $\text{Ni}(\text{OH})_2$ and $\text{Al}(\text{OH})_3$ [38]. Hence, right-shift from 1650 to 1600 cm^{-1} is caused by dehydration of layer-confined water molecules. Right-shift of the peak at 1420 cm^{-1} due to $\nu(\text{C-O})$ of carbonate anions arises from significantly enhanced anion – layer interactions after dehydration [37]. Very interestingly, all post **Stage I** dehydration samples present very similar DRIFTS spectra. This is because removal of water molecules from the interlayer space significantly reduces the chemical complexity of guest – host interactions among various intercalated (confined) species (mainly carbonates) and the NiAl-LDH layers. After complete interlayer dehydration, the high wavenumber broad peak spanning from 4000 to 2500 cm^{-1} becomes near-absent. The remaining peaks are mainly from the layer-possessed functional groups and charge-balancing carbonates.

Stage II degradation of the LDH structure from $\sim 200 \text{ }^\circ\text{C}$ concludes at $\sim 450 \text{ }^\circ\text{C}$ for NiAl-LDH-2 and at about $400 \text{ }^\circ\text{C}$ for NiAl-LDH-3 and 4, in which two significant transitions are detected by *in situ* DRIFTS. Specifically, the intensity of signal at 1370 cm^{-1} decreases as temperature increases, which strongly suggests decomposition of interlayer confined carbonate species to CO_2 that was also seen within the same temperature range in the TG-DSC-MS thermal analysis [33,36]. Meanwhile, the signal at $\sim 1600 \text{ cm}^{-1}$ completely disappears. According to the *in situ* XRD data, this is caused by thermal decomposition of $\text{Ni}(\text{OH})_2$ and $\text{Al}(\text{OH})_3$, and phase transition to NiO and Al_2O_3 (see **Figure 3** and **Figure S2**). This set of *in situ* DRIFTS data is in excellent agreement with TG-DSC-MS and *in situ* XRD results, which reveal a *two-stage degradation mechanism*, including **Stage I** interlayer dehydration leading to the loss of LDH's

interlayer gallery; and **Stage II** degradation of LDH layers with significant phase transition of all NiAl-LDH samples induced by the decomposition of the anionic charge-balancing carbonate species.

Figure 5. Enthalpies of formation from NiO (s), Al(OH)₃ (s), H₂O (l), and CO₂ (g) at 25 °C for all NiAl-LDH samples.

Figure 6. (a) Ni/Al ratio, (b) *d*-spacing reflecting interlayer spacing, (c) particle size for all NiAl-LDH samples, and (d) Brunauer-Emmett-Teller (BET) specific areas ^[21].

Figure 7. Energetic – structure – performance relationships for all NiAl-LDHs with Ni/Al from 2 to 4. The specific capacity (C_s) values were cited from reference ^[21].

Energetics of As-made and Dehydrated NiAl-LDHs

According to the TG-DSC-MS thermal analysis results, the integral enthalpies of hydration (ΔH_{hydr}) of NiAl-LDH samples are -68.68 ± 5.12 , -83.80 ± 4.81 and -83.32 ± 5.53 kJ/mol water, for NiAl-LDH-2, 3, and 4, respectively. The enthalpies of formation, ΔH_f , for NiAl-LDH samples from NiO, γ -Al(OH)₃, H₂O and CO₂, are calculated using the thermodynamic cycle listed in **Table S2** and **S3**. In general, formation of the as-made fully hydrated NiAl-LDHs is energetically favorable, reflected by the negative formation enthalpy (ΔH_f) values. ΔH_f tends to be less exothermic as the Ni/Al ratio or interlayer spacing increases, ranging from -59.00 ± 1.46 to -37.80 ± 5.37 kJ/mol Ni (see **Figure 5**). Further, with the enthalpies of formation and dehydration, we are able to calculate the formation enthalpies of dehydrated NiAl-LDH samples with the interlayer

confined water removed, ΔH_{f-dehy} . Surprisingly, all ΔH_{f-dehy} values are positive, strongly suggesting the dehydrated NiAl-LDH samples are energetically unfavorable. Moreover, ΔH_{f-dehy} becomes more endothermic as the Ni/Al ratio increases. Specifically, ΔH_{f-dehy} are 19.95 ± 6.06 , 31.50 ± 7.36 , and 35.26 ± 7.24 kJ/mol Ni for NiAl-LDH 2, 3 and 4, respectively (see **Figure 5**).

Energetic Landscape of NiAl-LDH, Critical Role of Water Intercalation, and Structure – Energetics – Performance Relationships

Our earlier study demonstrated that increase in Ni/Al ratio leads to (1) increase of Ni redox site concentration, (2) expansion of interlayer space (van der Waals gap), (3) degradation of crystallinity and morphology (see **Figure 1** and **3**), (4) enhancement of ion transport kinetics, and (5) modification of specific capacitance (F/g) with the highest capacity recorded for NiAl-LDH-3^[33]. All these trends are summarized in **Figure 6**. Using *in situ* methodologies and from a thermodynamic perspective, our present study leads to the following general conclusions: *first*, as the Ni content increases, both as-made (hydrated) and dehydrated NiAl-LDHs tend to be energetically less stable, and all dehydrated NiAl-LDH samples are no longer stable, reflected by the positive formation enthalpies (ΔH_{f-dehy}). Although decreased stability upon introduction of more redox defects is a common phenomenon seen for solid state oxide and hydroxide materials^[39–41], the endothermic enthalpies of formation for dehydrated NiAl-LDH are not typically seen, which indicates that upon removal of the intercalated water the NiAl-LDH is unstable and will readily transform to more energetically favorable phases. Hence, interlayer-confined species such as small molecules, ions, and/or materials are essential to minimize or neutralize the metastability generated by redox site enrichment. In other words, interlayer-confined species pay the “cost of being redox site rich”. *Second*, hydration plays critical thermodynamic roles in determination of the functionality of NiAl-LDH structures by (i) energetically maintaining the open interlayer

gallery structure for electrolyte intercalation with rapid kinetics; (ii) stabilizing the interlayer-confined charge-balancing carbonates by acting as solvents; and (iii) minimizing the metastability generated by highly concentrated layer-possessed hydroxyls in NiAl-LDHs. The energetic balance though subtle interplays between compositional factors and water – layer guest – host interactions governs the specific capacitance of NiAl-LDH materials (see **Figure 7**). *Lastly*, inspired by the thermodynamic insights into NiAl-LDH formation and hydration obtained here, we anticipate that we will be able to pay the “energetic cost of being redox site rich” by interfacial engineering strategies to tune the chemical nature and magnitudes of guest – host interactions to synthesize pseudocapacitive energy storage materials with enhanced stability, faster kinetics, and higher capacitance. Also, we expect that by tuning the degree of hydration we may manipulate the kinetics, energetics, and capacitance of TM-LDH materials to engineer desired qualities.

Conclusions

In our earlier study, we have shown that Ni atom enrichment for NiAl-LDH leads to expansion in interlayer spacing facilitating faster kinetics and increased number of energy storage sites during the reversible charge – discharge process. Here, from a thermodynamic perspective, we further the fundamental understanding of the NiAl-LDH system by demonstrating that the increase in Ni redox site concentration results in *decreased energetic stability* for both as-made (hydrated) and dehydrated NiAl-LDHs, reflected by their *enthalpies of formation*. Moreover, interlayer hydration significantly stabilizes the metastability introduced by Ni enrichment. The highest specific capacity observed for NiAl-LDH-3 (2128 F/g at 1 A/g) with an intermediate Ni content is achieved by effective stabilization from hydration through *subtly balanced interlayer confinement (intercalation) and interfacial binding*, which intrinsically pays the “energetic cost” generated by the increase of the Ni/Al ratio. Therefore, our study highlights the critical role of

hydration, and demonstrates that interfacial engineering on the nanoscale within the interlayer space is a promising strategy to finetune the confinement chemistry and surface redox sites for substantial enhancement of the energy storage properties of transition metal layered double hydroxides (TM-LDHs).

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