

Insights into the electrochemistry of layered double hydroxide containing cobalt and aluminum elements in lithium hydroxide aqueous solution

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Abstract

The electrochemical capacitive behavior of layered double hydroxide containing cobalt and aluminum (Co–Al LDH), synthesized by a “memory effect” route, was in detail evaluated by cyclic voltammetry (CV) and chronopotentiometry in 1 M LiOH aqueous electrolyte. A specific capacitance of 187 F g^{-1} was obtained even after 1000 cycles at a current of 2 A g^{-1} . Moreover, it was found that Co–Al LDH undergoes two independent electrode processes in LiOH aqueous solution, involving the simultaneous intercalation of an ion-pair, i.e. lithium cation and hydroxyl group, which is different from the mechanisms in NaOH and KOH aqueous solutions. The possible reason is thought to be the selective intercalation into Co–Al LDH for alkali metal ions due to their respective ionic radius. Only the cation with appropriate size is suited for inserting into $[\text{Co}(\text{OH})_6]$ or $[\text{Al}(\text{OH})_6]$ octahedral vacancies.

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1. Introduction

Layered double hydroxides (LDHs), also called as anionic clay and hydrotalcite-like compounds, are a unique family of compounds. They are generally viewed as derivatives from lamellar brucite $\text{Mg}(\text{OH})_2$. When a part of Mg^{2+} ions are isomorphously replaced by trivalent metallic cations, the slab layer bears excess positive charge, which is balanced by negative-charge anions occupying the interlayer spaces. In the layers constituted by edge-sharing $[\text{M}(\text{OH})_6]$ octahedra, metal atoms associate with hydroxyls via covalent bond while anions and water molecules in the interlayers are united by hydrogen-bond and van der Waals interaction. Owing to the weak interaction between anions and slab layers, the anions are exchangeable. Many divalent metal ions, such as Ni^{2+} , Co^{2+} , Mn^{2+} , Zn^{2+} , Cu^{2+} , and trivalent ones like Al^{3+} , Cr^{3+} , can cooperate to form layered double hydroxides as long as their radii are close to Mg^{2+} ion.

Layered double hydroxides have become a subject of considerable interest due to their unique structural anisotropy. Many

studies have addressed on LDHs as ion-exchangers, catalysts, catalyst supports, flame retardants, and slow medicine-releaser [1–5]. And more and more novel applications are being developed, based on the high anisotropy in their chemical bondings. Recently, for example, Li et al. [6] used LDHs as the precursor for the preparation of carbon nanotubes. In electrochemical field, its application can trace back to the usage of layered double hydroxides in analysis, electrocatalysis, and chemical sensors [7–14]. More recently, Zhang and co-workers [15–17] reported the investigation on LDHs containing transitional metal as the electrode materials for supercapacitor. Wang et al. [18] studied the electrochemical properties of double oxides obtained from the annealing of LDHs. Leroux et al. [19] employed LDHs as template to synthesize mesoporous carbon for supercapacitor. All above researches show that LDHs have great potential in supercapacitor as a promising candidate for electrode materials.

In the early studies on LDHs for supercapacitors, the electrolytes used were generally aqueous solutions of KOH or NaOH. However, little effort has been given to the systematic investigation of electrochemical behaviors in alkaline solutions, including in LiOH solution. Some recent researches [20–22] have confirmed that the assembly of a hybrid capacitor, con-

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taining materials with different nature as electrodes, is very promising for the enhancement of capacitance and energy density, in which the electrolytes containing lithium ion were always used. In our early work [23], we have prepared Co–Al LDH by direct coprecipitation, investigated its electrochemical behavior in 1 M KOH solution in detail, and compared it with the restacked Co–Al LDH via a method of so-called “memory effect”, in which a three-step procedure of coprecipitation, annealing, and reconstruction was involved. It was found that Co–Al LDH obtained through the route of “memory effect” had more regular crystal and better electrochemical properties in 1 M KOH solution than the as-prepared one. Therefore, in this paper, we focus our attention on the study of electrochemical capacitive behavior of Co–Al LDH in aqueous LiOH solution with an intention to obtain full insight on the behaviors of Co–Al LDH in alkaline solutions. The material was studied by cyclic voltammetry and constant current charge/discharge tests. To understand the electrochemistry of Co–Al LDH in LiOH solution, the role of lithium ion is discussed in detail. As comparison, the electrochemical behaviors of Co–Al LDH in KOH and NaOH solutions are also presented, respectively.

2. Experimental

A solid Co–Al LDH was synthesized through a three-step method of direct coprecipitation, sintering and reconstruction, according to the procedure described in detail previously, which is on the basis of direct coprecipitation method [24] with a little modification. The prepared compound was used here as starting material to study its electrochemical properties in LiOH solution via cyclic voltammetry and chronopotentiometric technique. For comparison, its electrochemistry in NaOH and KOH solutions was also investigated. The electrochemical system employed here was a conventional three-electrode one, in which a Pt foil of 1 cm² and a saturated calomel electrode (SCE) acted as counter and reference electrodes, respectively. The preparation of the study electrode was the same as the one reported by our group [23]. All potentials are reported versus SCE in the solvent used. All electrochemical tests were carried out at room temperature and recorded by a CHI 660B electrochemical workstation system.

3. Results and discussions

Chronopotentiometric experiments were carried out in 1 M LiOH aqueous solution at various current densities. The acquired data are depicted in Fig. 1(a) and the specific capacitances (C_s)

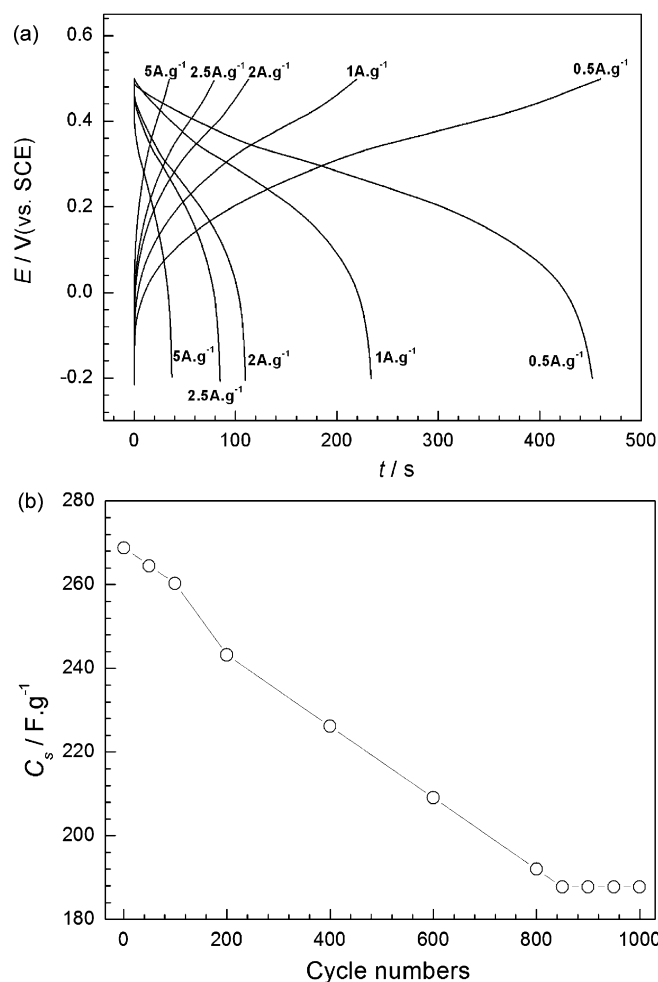


Fig. 1. The chronopotentiogram at various currents (a); and the relationship between the specific capacitance and cycles at 2 A g⁻¹ (b), of the Co–Al LDH sample in 1 M LiOH aqueous solution.

calculated from Eq. (1) [21,25,26] are listed in Table 1.

$$C_s = \frac{I\Delta t}{m\Delta V} \quad (1)$$

It can be seen that C_s still maintains about 300 F g⁻¹ even if the current increases from 0.5 to 2.5 A g⁻¹, and that the discharge/charge efficiency is more than 92%, indicating good reversibility and high capacitance at large current density. The discharge/charge measurement at a large current of 2 A g⁻¹ was performed in order to evaluate the long-term stability of the Co–Al LDH (shown in Fig. 1(b)). In the first cycle, the specific capacitance is as high as 268 F g⁻¹. Then it decreases with

Table 1
The specific capacitance of the Co–Al LDH at various current in 1 M LiOH aqueous solution

Current density (A g ⁻¹)	Charge capacitance (F g ⁻¹)	Discharge capacitance (F g ⁻¹)	Charge/discharge efficiency (%)
0.5	328	322	98.3
2.0	322	314	97.3
2.5	302	281	92.9
5.0	267	267	100

cycles till about the 800th cycle. From 850 to 1000 cycles, an interesting phenomenon occurs that the declining tendency of the specific capacitance with cycle halts and the C_s value keeps constant at 187 F g^{-1} . The possible reason will be discussed later.

Fig. 2(a) gives the cyclic voltammetry of the Co–Al LDH at a scan rate of 5 mV s^{-1} in 1 M LiOH solution. A set of redox waves appear at the potentials of 410 and 225 mV versus SCE in the first cycle, which can be ascribed to the conversion between Co(+2) and Co(+3). From 2 to 8 cycles, however, the anodic peak current decreases almost half and the shapes of the peaks become broader than before. These changes may imply the occurrence of a different electrode process after the first cycle. There is another interesting phenomenon in the CV curve at a scan rate of 5 mV s^{-1} after the electrode has undergone 1000 cycles of charge/discharge in 1 M LiOH aqueous solution at a large current of 2 A g^{-1} (shown in Fig. 2(b)). Compared with the CV curve before the cycles, the broad redox peaks become sharper, also indicating another different electrode process from the one before the cycles.

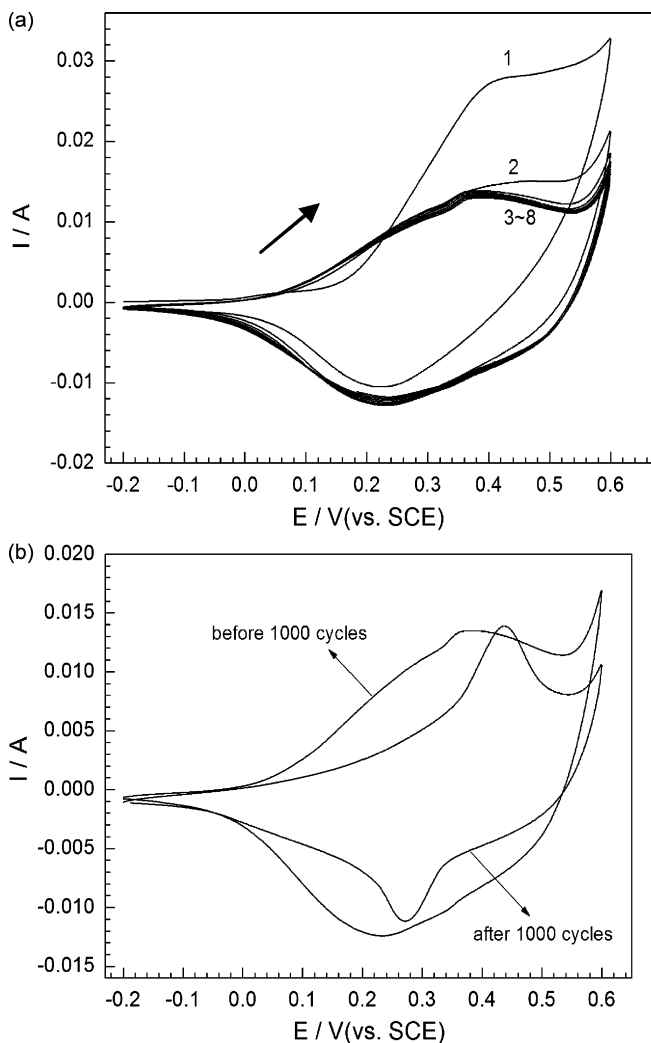


Fig. 2. The cyclic voltammograms of the material of Co–Al LDH at a scan rate of 5 mV s^{-1} before (a) and after (b) 1000 cycles of constant current charge/discharge test in 1 M LiOH aqueous solution.

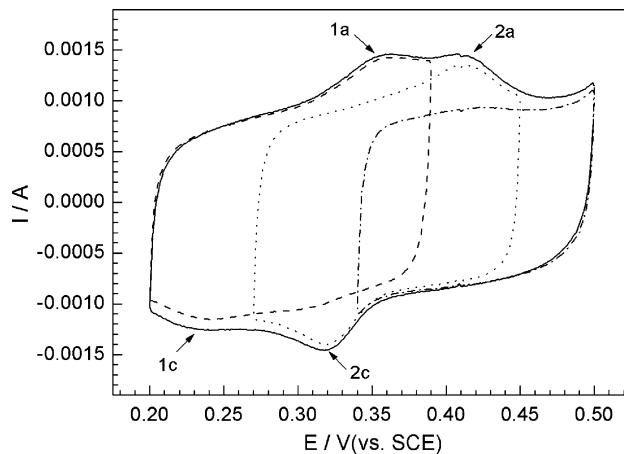


Fig. 3. The cyclic voltammograms of the Co–Al LDH at a scan rate of 0.5 mV s^{-1} in 1 M LiOH aqueous solution.

In order to explain the above interesting phenomena observed, cyclic voltammetry at a slow scan rate of 0.5 mV s^{-1} was carried out in 1 M LiOH solution and shown in Fig. 3. There are two pairs of defined redox waves, marked as $1a/1c$ and $2a/2c$, respectively. Before discussing the origin of the two couples, it is necessary to decide whether they are dependent or not. When the potential scans between 200 and 390 mV versus SCE, peaks $1a$ and $1c$ still appear while peak $2c$ disappears, showing that peak $2c$ is independent on peaks $1a/1c$, i.e., the product of peak $1a$ is reduced at the potential for peak $1c$. Changing potential range from 270 to 450 mV versus SCE, peaks $2a$ and $2c$ appear but $1a$ disappears, meaning that $1a$ does not result from the oxidation of the peak $2c$. In addition, all peaks disappear when scanning from 340 to 500 mV. Based on the above analysis, it can be concluded that two pairs of peaks $1a/1c$ and $2a/2c$ are two redox couples, and that the electrode processes for above redox couples are independent on each other.

We believe that the redox peaks $2a$ and $2c$ in the CV curves are ascribed to the oxidation and reduction of cobalt element in the Co–Al LDH material. Scavetta et al. [13] had the similar observation that a pair of redox waves appeared between 400 to 500 mV versus SCE in 0.1 M NaOH solution at a scan rate of 5 mV s^{-1} in their research of Co–Al LDH as catalyst. They thought the peak system was related to the reaction written as Eq. (2):



Here, HT stands for hydrotalcite-like structure.

In order to verify whether the process for $2a/2c$ is related to Eq. (2), cyclic voltammeteries in LiOH solutions of various concentrations were carried out. The dependence of the formal potential (E_f) on the concentration of OH^- ion is shown in Fig. 4(a). Formal potential is calculated [27] approximately from $(E_{a,p} + E_{c,p})/2$, where $E_{a,p}$ and $E_{c,p}$ stand for anodic and cathodic peak potentials in CV curves, respectively. The scan rates used are all 0.5 mV s^{-1} . The linear relation of E_f to $\log C_{\text{OH}^-}$ is clearly observed, but the slope is negative, indicating that the formal potential decreases with the concentrations of OH^- ion. According to Nernstian law and Eq. (2), the formal potential for

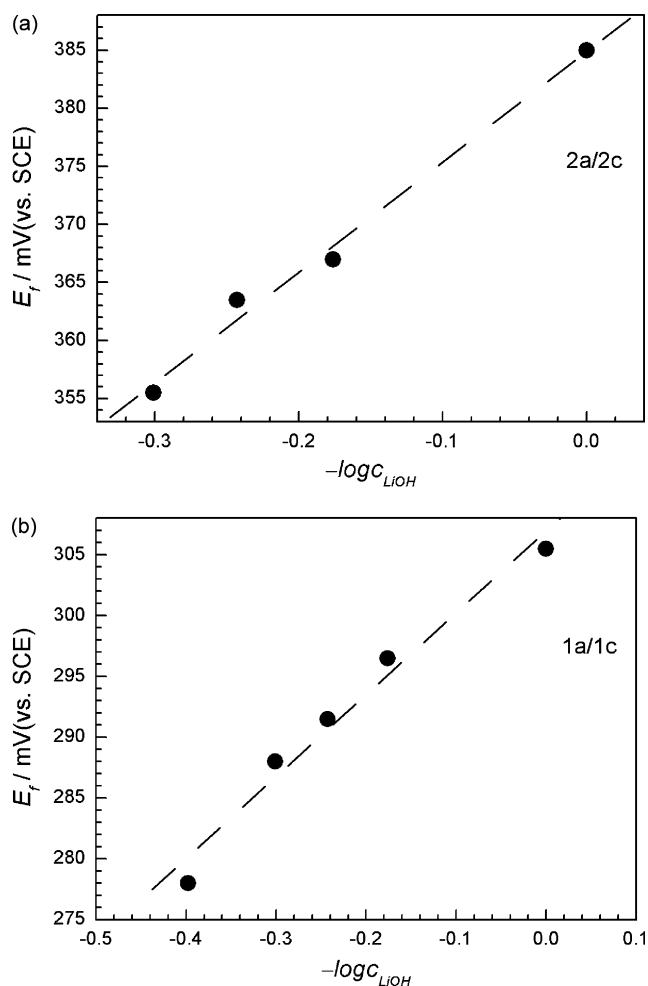


Fig. 4. Plot of E_f versus $\log C_{OH^-}$ for the Co–Al LDH in LiOH solution of various concentrations. 2a/2c; (b) 1a/1c.

the couple 2a/2c can be written as

$$E_{2f} = E_2^0 - 0.059 \log a_{OH^-} \quad (3)$$

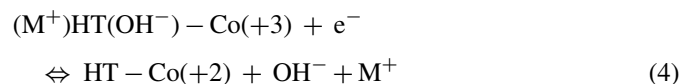
The result shown in Fig. 4(a) is in good accordance with Eq. (3). So, the reaction for 2a/2c involves the insertion/deinsertion of OH^- ions into Co–Al LDH, resulting in the conversion of Co(+2)/Co(+3).

The formal potential for the conversion of Co(+2)/Co(+3) in our work is not in complete accordance with the values in literatures. For examples, E_f is 89 mV for $LiCoO_2/LiHCoO_2$ and 200 mV (versus Ag/AgCl) for $Co(OH)_2/CoOOH$ in 1 M KOH solution [28,29], respectively. There were also reports [18,30] that the potential for $Co(OH)_2/CoOOH$ was in the range of 150–300 mV (versus Hg/HgO). The differences may result from the nature of different materials, in which the coordination circumstance of Co-element varies in the respective material. In Co–Al LDH, owing to the partial substitution of trivalent metal element to divalent one, the coordinating condition differs from that in $Co(OH)_2$. So, it is reasonable to believe that the insertion product of OH^- for Co–Al LDH in 1 M LiOH solution is not the oxyhydroxide form of Co element but complex with Al element.

As far as the couple 1a/1c is concerned, we think that they are very probably due to the insertion/deinsertion of lithium ion in Co–Al LDH. It is well known that layered double hydroxides are composed of brucite-structure slabs and anions occupying the interlayer space. In general, they are classified into two types. One sort is characterized as the substitution of a fraction of divalent metallic element by trivalent one, resulting in an excess of positive charge on the slab layers, which is balanced by interlayer anions. Except this, there is another unique sort of LDH containing lithium element and one trivalent metallic ion [31], such as $LiAl_2(OH)_6Cl \cdot nH_2O$, in which Li^+ cations occupy the cave space of octahedral $[Al(OH)_6]$.

In Li–Al LDH, the brucite layer slabs are composed of octahedral $[Al(OH)_6]$ in which nearly close packed hydroxyls form $(OH)_6$ octahedra and two-thirds of the octahedral holes are occupied by Al^{3+} cations [32–34]. The remaining third of the vacant octahedral sites are filled by Li^+ ions, resulting in the excess positive charge in the hydroxide sheets. Interestingly, Li^+ cation can insert into or extract out of octahedral $[Al(OH)_6]$, accompanied by Cl^- anion simultaneously [35,36]. This phenomenon of co-intercalation of ion-pair was also observed in the study of a Ni–Al based hydrotalcite [37,38], in which hexacyanoferrate(II) and potassium cation united as an ion-pair for insertion and deinsertion. Therefore, in the material of Co–Al LDH, there is also probability for Li^+ ion to fill in the vacuum site of $[Co(OH)_6]$ or $[Al(OH)_6]$ octahedral vacancies just like in the case of $LiAl_2(OH)_6Cl$.

If we suppose that the couple for the redox waves 1a/1c result from the intercalation of alkali metal ions (M^+) into the slab of Co–Al layered double hydroxide with hydroxyls together, a general equation can be written as following:



According to Nernstian law and Eq. (4), the formal potential of the couple 1a/1c depends on the activity of the lithium hydroxide:

$$E_{1f} = E_1^0 - 0.059 \log a_{LiOH} \quad (5)$$

It is proved to be the case by the straight line of E_f versus $\log C_{LiOH}$ with a negative slope (see Fig. 4(b)). So, two different electrode processes take place for Co–Al LDH in alkaline LiOH solution, one resulting from the conversion of Co(+2)/Co(+3) and the other involving the insertion/deinsertion of both OH^- and Li^+ ions.

In the foregoing discussion, we mentioned the difference in the CV curve of the Co–Al LDH between the first and followed cycles in Fig. 2(a). Given above assumption of the insertion of Li^+ ion into LDH, the seemingly strange behavior can be explained reasonably: in the 1st cycle, when scanning began forth wards (from negative to positive potential), only hydroxyl intercalated. When scanning in the 2nd cycle, Li^+ ion began to insert into and extract out of the lattice of the Co–Al LDH with hydroxyl together, resulting in the difference between the first and followed cycles. So, there are two kinds of processes undergoing in the followed cycles, including Faradic reaction

and the insertion/deinsertion of Li^+ ion, whose characteristic is the broader peaks in CV curve. Accordingly, the specific capacitance of Co–Al LDH in 1 M LiOH solution is 268 F g^{-1} , bigger than that in 1 M KOH solution (145 F g^{-1}).

The process for insertion/deinsertion of Li^+ ion may be unstable, which can be proved by chronopotentiometric experiment and CV curves (see Figs. 1(b) and 2(b)). After 800 cycles of charge/discharge at a constant current of 2 A g^{-1} in 1 M LiOH solution, C_s maintained at 187 F g^{-1} between 850 and 1000 cycle, resulting from the insertion of Li^+ ion into Co–Al LDH completely and the formation of a new stable compound similar to $\text{LiAl}_2(\text{OH})_6\text{Cl}$. The conclusion can be proved to be logical by CV curve after 1000 cycles at 2 A g^{-1} , which is comparable to the one for Co–Al LDH after 1000 cycles at 2 A g^{-1} in 1 M KOH solution (see Fig. 5). The peaks at the potential of 437 and 273 mV versus SCE belong to the redox couple of $\text{Co}(+2)/\text{Co}(+3)$. At this stage, there is already no main contribution from insertion/deinsertion of Li^+ ions. That is why the waves at 437 and 273 mV versus SCE in the cyclic voltammogram become sharp.

In order to test whether the reaction mechanism suggested above is right or not, the Co–Al LDH sample was charged and discharged for 100 cycles at a constant current of 1 A g^{-1} in 1 M LiOH solution. After rinsing with ultrapure water and drying in air, the electrode was tested using XRD technique. The XRD patterns of the Co–Al LDH before and after the cycles are shown in Fig. 6. Besides the reflections at the 2θ values of 44.5° and 51.9° which belong to the planes (1 1 1) and (2 0 0) of the collector of Ni grid (JCPDS: 04-0850), no new diffraction peaks appear except the shift of the peaks for the planes (0 0 3) and (0 0 6) of LDH, indicating the maintenance of the layered structure after the constant-current charge/discharge test. Accordingly, the values of d_{003} and d_{006} become smaller after the cycling than before, implying that the interlayer distance becomes narrow. After careful consideration, we think that it, firstly, does not result from the influence from carbonate ions in that there are already carbonate intercalating into the interlayer spaces of the Co–Al LDH [23] before the cycling. Secondly, the

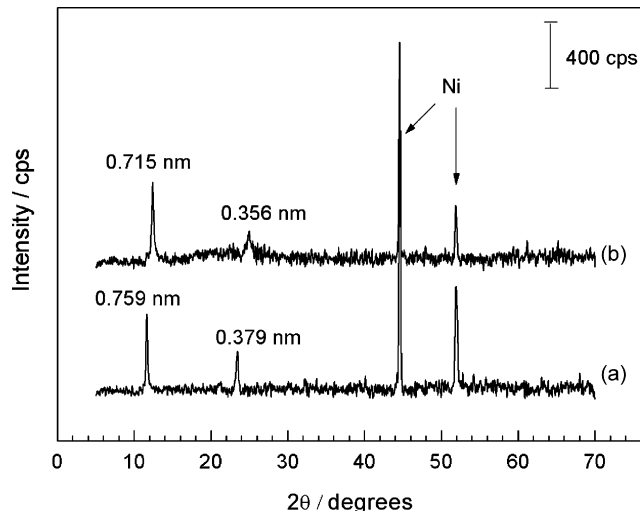


Fig. 6. The XRD patterns of the Co–Al LDH before (a) and after (b) the 100 cycles of charge/discharge at a constant current of 1 A g^{-1} in 1 M LiOH solution.

shifts of the reflections do not result from the replacement of hydroxide groups for carbonate ions in the interlayer because of carbonate's exceptionally higher affinity to LDHs [39] than other anions (OH^- , Cl^- , etc.). Therefore, the reflection shifts, meaning the reinforce of the interaction between the host slabs and the interlayer anions, can only come from the insertion of lithium ions into the lattice of the Co–Al LDH, which brings more positive charges to the slabs and, consequently, shortens the interlayer distance.

It should be pointed out that there are two redox couples in LiOH solution whereas only one set of redox waves appeared in NaOH and KOH solutions, which can be clearly observed in the cyclic voltammograms at a scan rate of 0.5 mV s^{-1} (shown in Fig. 7). In order to explain the difference, it is very necessary to make clear the correlation of $1a/1c$ and $2a/2c$ peaks in LiOH solution with the waves appeared in NaOH and KOH solutions. In our early work, the formal potentials of the Co–Al LDH in 0.5, 0.67, 0.8, and 1 M KOH solutions are 374.4, 355.3, 348.2, and 337.5 mV, respectively. For comparison, the formal potentials

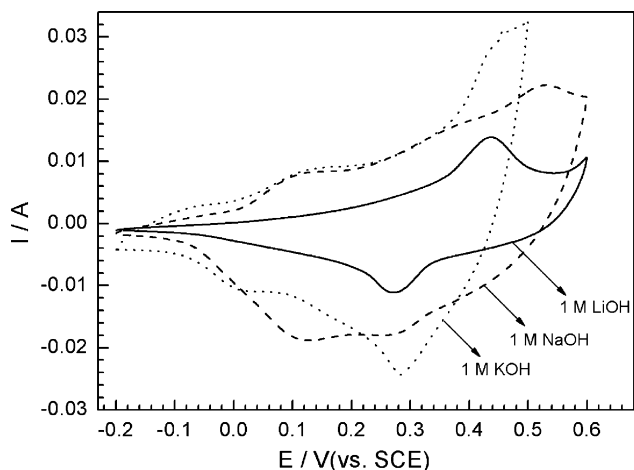


Fig. 5. Cyclic voltammograms of the Co–Al LDH at a scan rate of 5 mV s^{-1} after 1000 cycles of charge/discharge in different electrolyte solutions.

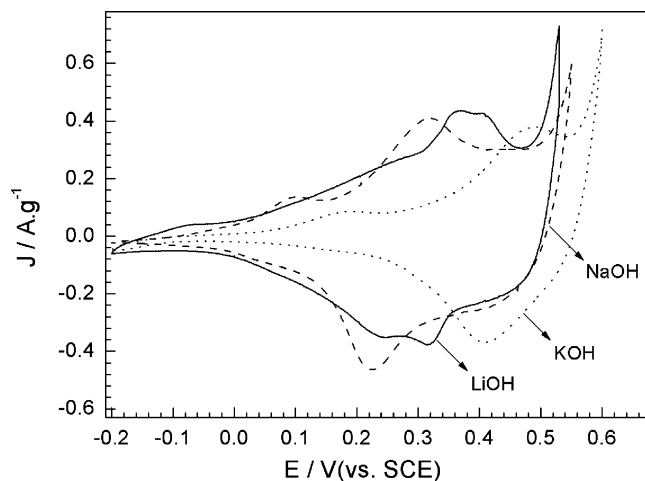


Fig. 7. The cyclic voltammograms of Co–Al LDH in 1 M alkaline solutions at a scan rate of 0.5 mV s^{-1} .

Table 2
The formal potentials of the Co–Al LDH in LiOH and NaOH solutions of various concentrations

Electrolyte	C (M)	$E_{1a,p}$ (mV)	$E_{1c,p}$ (mV)	E_{1f} (mV)	$E_{2a,p}$ (mV)	$E_{2c,p}$ (mV)	E_{2f} (mV)
NaOH	1.00	319.0	225.0	272.0			
	1.25	298.0	206.0	252.0			
	1.50	271.0	215.0	243.0			
	2.00	248.0	182.0	215.0			
LiOH	1.00	357.0	254.0	305.5	425.0	345.0	385.0
	1.50	243.0	350.0	296.5	403.0	331.0	367.0
	1.75	225.0	358.0	291.5	399.0	328.0	363.5
	2.00	220.0	356.0	288.0	395.0	316.0	355.5
	2.50	273.0	283.0	278.0	373.0	284.0	328.5

of the Co–Al LDH in LiOH and NaOH solutions with various concentrations are also listed in Table 2. It can be seen that the formal potential E_{2f} for $2a$ and $2c$ peaks in 1 M LiOH is close to the one in 1 M KOH solution, which attributes to the transversion of Co(+2)/Co(+3). The negative slopes of E_f versus $\log C_{OH^-}$ are both in accordance with Eq. (2), indicating that $2a$ and $2c$ peaks in 1 M KOH share the same mechanism as in 1 M LiOH solution.

To our surprise is that the electrochemical behavior for the Co–Al LDH in sodium hydroxide is greatly different from the cases in lithium hydroxide and potassium hydroxide solutions. The formal potential E_f in 1 M NaOH solution is very close to the one for $1a/1c$ couple in 1 M LiOH solution. No waves for $2a/2c$ couple were observed. The dependence of the formal potential (E_f) on the concentration of NaOH is also shown in Fig. 8 to have a clear observation. The straight line plot for E_f versus $\log C_{NaOH}$ also has a negative slope. And the specific capacitance decreases with cycling of charge/discharge. All these results lead us to believe that the reaction in 1 M NaOH solution is similar to the process for $1a/1c$ couple in 1 M LiOH solution. Namely, hydroxyl group intercalates with sodium cation simultaneously. However, after 1000 cycles of charge and discharge, two peaks at 530 and 273 mV versus SCE appear in Fig. 5, which is ascribed to the redox couple of Co(+2)/Co(+3). Obviously, it resulted from the formation of

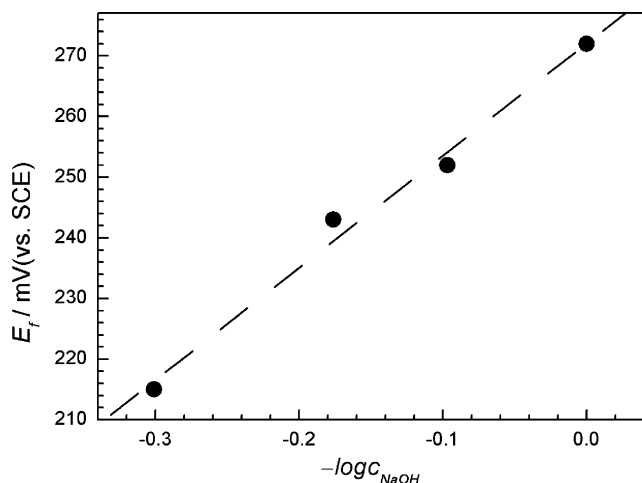


Fig. 8. Dependence of E_f on $\log C_{NaOH}$ in NaOH electrolyte solution of various concentrations.

a stable intercalation compound just like the case in 1 M LiOH solution.

As regard to the absence of co-insertion of potassium ion and hydroxyl in KOH solution, our explanation is that the intercalation of alkali metal ions into Co–Al LDH depends heavily on their respective ionic radius. If we ignore the small structural distortion derived from the substitution of OH^- ions for O^{2-} ions in an octahedral $[Co(OH)_6]$ or $[Al(OH)_6]$ and still regard it as a close packed $[CoO_6]$ or $[AlO_6]$ octahedron in Co–Al LDH, a simple calculation can be given and an interesting result is acquired. The radii for Li^+ , Na^+ , and K^+ cations are 0.68, 0.95,

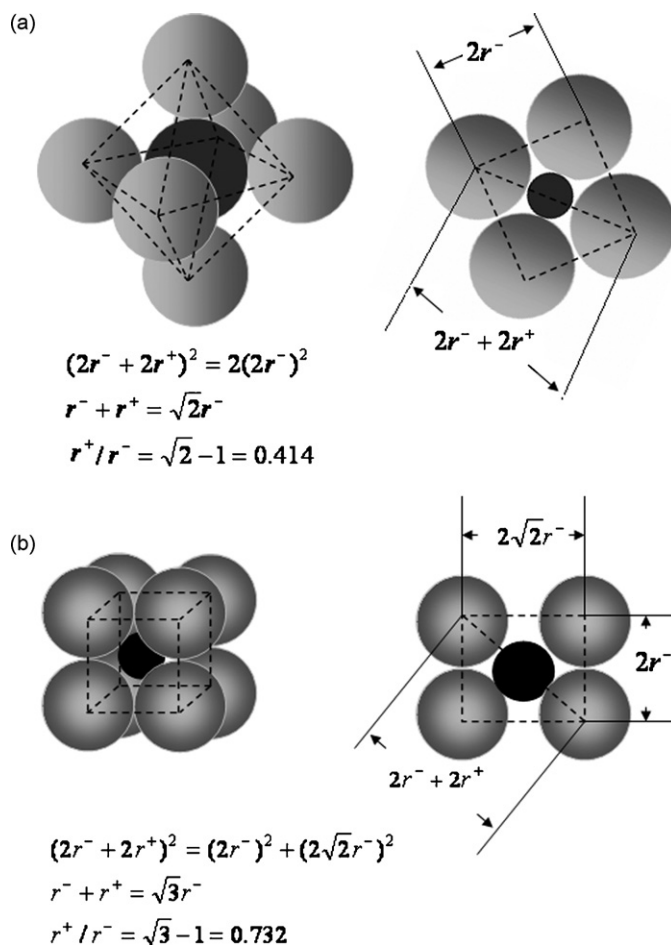


Fig. 9. Illustrations of the lower limit values of coordination polyhedra coordination number: (a) $n=6$, (b) $n=8$.

and 1.33 Å, respectively, while the radius for O^{2-} ion is 1.40 Å. Among the three alkali metal ions, the values of $r(M^+)/r(O^{2-})$ for Li^+ and Na^+ ions are between 0.414 and 0.732 while for K^+ ion it is bigger than 0.732. According to crystallography, the value of r^+/r^- has a great role in the construction of a stable crystal (shown in Fig. 9). When it is equal to or bigger than 0.414 which is the lower limit value of r^+/r^- for octahedral structure, the number of coordination (n) is 6. When it beyonds 0.732, the lower limit value of r^+/r^- for cubic structure, the coordination number increases to be 8. Thus, when the value of r^+/r^- is between 0.414 and 0.732, octahedral structure can exist stably. Namely, only the cation with appropriate size can insert into the vacant octahedral sites of Co–Al LDH. So, only Li^+ and Na^+ cations are suitable ions for intercalating in the remaining vacancies of $(OH)_6$ octahedra. Compared with lithium and sodium cations, potassium ion has too large radius to fill into the $[Co(OH)_6]$ or $[Al(OH)_6]$ octahedral vacancies.

4. Conclusions

Lamellar Co–Al LDH was prepared by a “memory effect” route. Its electrochemical behavior in LiOH aqueous solution was investigated by cyclic voltammetry and constant-current charge/discharge techniques in detail. After 1000 cycles at a large current of $2 A g^{-1}$ in 1 M LiOH solution, the lamellar Co–Al LDH still showed larger capacitance than in 1 M KOH solution, indicating a promising candidate for electrode material of supercapacitor. It was also found that there are two electrode processes for Co–Al LDH in LiOH solution, including the redox conversion of $Co(+2)/Co(+3)$ and the insertion of lithium cation and hydroxyl as an ion-pair into the lattice of the Co–Al LDH material, which differs from the mechanisms in NaOH and KOH solutions. We believe that whether an alkali metal ion intercalates into Co–Al LDH or not is decided by its ionic radius. Only the one with appropriate size is suited for the insertion into $[Co(OH)_6]$ or $[Al(OH)_6]$ octahedral vacancies.

Acknowledgements

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