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# **ORIGINAL ARTICLE**

# Direct preparation of Al-substituted $\alpha$ -Ni(OH)<sub>2</sub> from Al-containing salt solution by immersing method

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# KEYWORDS

pure α-Ni(OH)<sub>2</sub>; AlCl<sub>3</sub> solution; AlCl<sub>3</sub>-Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution; Directly immersing; Al-substituted α-Ni(OH)<sub>2</sub> **Abstract** The present study attempts to prepare Al-substituted  $\alpha$ -Ni(OH)<sub>2</sub> and Al-substituted  $\alpha$ -Ni (OH)<sub>2</sub> with modified interlayer anions by directly immersing pure  $\alpha$ -Ni(OH)<sub>2</sub> into AlCl<sub>3</sub>-containing solutions. XRD and FT-IR analysis demonstrated Al-substituted  $\alpha$ -Ni(OH)<sub>2</sub> can be prepared directly by soaking pure  $\alpha$ -Ni(OH)<sub>2</sub> into AlCl<sub>3</sub> solution. Al-substituted  $\alpha$ -Ni(OH)<sub>2</sub> with S<sub>2</sub>O<sub>3</sub><sup>2-</sup> as the primary anion in the interlayer can be obtained by immersing pure  $\alpha$ -Ni(OH)<sub>2</sub> into AlCl<sub>3</sub>-Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution. The analysis of Al content in samples demonstrated the Al content in the Alsubstituted  $\alpha$ -Ni(OH)<sub>2</sub> was regulated by adjusting the molar ratio of pure  $\alpha$ -Ni(OH)<sub>2</sub> soaked in the solution and Al<sup>3+</sup> dissolved in the solution. The Al element entered the lattice of pure  $\alpha$ -Ni (OH)<sub>2</sub> through a process of pure  $\alpha$ -Ni(OH)<sub>2</sub> dissolved followed by the precipitation of Al<sup>3+</sup>, Ni<sup>2+</sup> and OH<sup>-</sup>. The S<sub>2</sub>O<sub>3</sub><sup>2-</sup> entered the interlayer of Al-substituted  $\alpha$ -Ni(OH)<sub>2</sub> through the formation process of the Al-substituted  $\alpha$ -Ni(OH)<sub>2</sub> or though ion exchange with the intercalated Cl<sup>-</sup>. The strongly alkaline solution soaking results demonstrated that Al-substituted  $\alpha$ -Ni(OH)<sub>2</sub> prepared by soaking pure  $\alpha$ -Ni(OH)<sub>2</sub> into AlCl<sub>3</sub>-containing solutions could preliminary get stabilized in the strongly alkaline solution.

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#### 1. Introduction

Due to excellent electrochemical properties, Ni(OH)<sub>2</sub> offers wide applications in sensors for drugs, electrochromic devices, Ni-based batteries, and supercapacitors (Ortiz et al., 2014; Nai et al., 2013; Andrade et al., 2018; Ash et al., 2006; Wang et al., 2014). Ni(OH)<sub>2</sub> exists in two crystal forms of  $\alpha$  and  $\beta$  (Gao and Jelle, 2013; Bao et al., 2013). As shown in Eqs. (1) and (2), OH<sup>-</sup> was taken up from the solution during the oxidation process from Ni(OH)<sub>2</sub> to NiOOH (Nai et al., 2013; Fang et al., 2019). As a result, the working environment of Ni(OH)<sub>2</sub> is usually strongly alkaline (Gao and Jelle, 2013; Bao et al., 2013;

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Fang et al., 2019). In the oxidation process of Ni(OH)<sub>2</sub>,  $\alpha$ -Ni(OH)<sub>2</sub> and  $\beta$ -NiOOH can be separately oxidized to  $\gamma$ -NiOOH (Eq. (1)) and  $\beta$ -NiOOH (Eq. (2)) (Yao et al., 2013; Jayashree and Vishnu, 2001; Li et al., 2018). More electrons transferred in the conversion of  $\alpha$ -Ni (OH)<sub>2</sub> to  $\gamma$ -NiOOH leads to higher energy conversion and higher valence state of Ni element was predicted from this path, making  $\alpha$ -Ni(OH)<sub>2</sub> more critical than  $\beta$ -Ni(OH)<sub>2</sub> (Huang et al., 2018; Li et al., 2010; Zhang et al., 2021). However, the easily conducted conversion of  $\alpha$ -Ni(OH)<sub>2</sub> to  $\beta$ -Ni(OH)<sub>2</sub> in strongly alkaline solutions permits its wide applications (Li et al., 2018; Jayashree and Kamath, 2011).

$$\alpha - \operatorname{Ni}(\operatorname{OH})_2 + \operatorname{OH}^- \rightleftharpoons \gamma - \operatorname{Ni}\operatorname{OOH} + \operatorname{H}_2\operatorname{O} + e \tag{1}$$

$$\beta - \text{Ni}(\text{OH})_2 + \text{OH}^- \rightleftharpoons \beta - \text{Ni}OOH + H_2O + e$$
 (2)

To improve the stability of  $\alpha$ -Ni(OH)<sub>2</sub> in strongly alkaline solutions, a method involving the substitution of the Ni atoms in the lattice of α-Ni(OH)<sub>2</sub> with other metal atoms was developed (Nethravathi et al., 2007; Chen et al., 2002). Among the substituting metals, Al stands out for its cheapness and high stability at trivalent state (Pan et al., 2003; Hu et al., 2011). The preparation process of Alsubstituted  $\alpha$ -Ni(OH)<sub>2</sub> involves the precipitation of Ni<sup>2+</sup> and Al<sup>3+</sup> (Li et al., 2016). The solubility product constant  $(K_{sn})$  for Ni(OH)<sub>2</sub> and Al(OH)<sub>3</sub> were  $5.5 \times 10^{-16}$  and  $1.3 \times 10^{-33}$ , respectively. Further, the  $K_{sp}$  for Al-substituted  $\alpha$ -Ni(OH)<sub>2</sub> was between Al(OH)<sub>3</sub> and Ni  $(OH)_2$ . A significant difference was seen between the  $K_{sp}$  of Ni $(OH)_2$ and Al(OH)<sub>3</sub>. Consequently, Gualandi reported that Eq. (3) takes place first, followed by Eq. (4) in a solution with a low  $OH^{-}/Ni^{2+}$ - $Al^{3+}$  ratio, while in a high ratio of  $OH^{-}/Ni^{2+}-Al^{3+}$ , only Eq. (4) takes place (Gualandi et al., 2015). In addition, the initially formed Al(OH)<sub>3</sub> in solutions with low OH<sup>-</sup>/Ni<sup>2+</sup>-Al<sup>3+</sup> ratio was dissolved following Eq. (5). Therefore, monitoring the  $OH^{-}/Ni^{2+}-Al^{3+}$  ratio in the solution is vital to prepare Al-substituted  $\alpha$ -Ni(OH)<sub>2</sub> with required amount of Al.

$$Al^{3+} + 3OH^{-} \rightleftharpoons Al(OH)_{3}$$
 (3)

$$(1 - x)Ni^{2+} + xAl^{3+} + 2OH^{-} + xA^{n-} + mH_2O \rightleftharpoons Ni_{1-x}Al_x(OH)_2A_x \cdot mH_2O(A^{n-} = NO_3^{-}, Cl^{-}, SO_4^{2-}etc.)$$
(4)

$$Al(OH)_3 + OH^- \rightleftharpoons AlO_2^- + 2H_2O \tag{5}$$

Chemical precipitation and electrodeposition are two commonly used methods to synthesize Al-substituted  $\alpha$ -Ni(OH)<sub>2</sub>. Vishnu Kamath synthesized Al-substituted  $\alpha$ -Ni(OH)<sub>2</sub> via chemical precipitation method using Ni(NO<sub>3</sub>)<sub>2</sub>-Al(NO<sub>3</sub>)<sub>3</sub> and NaOH solutions, and the total duration were more than 12 h (Zhang et al., 2021). Shangguan prepared Al-substituted  $\alpha$ -Ni(OH)<sub>2</sub> from a mixed salt solution of Ni<sup>2+</sup> and Al<sup>3+</sup> via chemical precipitating, and over 24 h were used (Shangguan et al., 2015). The OH<sup>-</sup>/Ni<sup>2+</sup>-Al<sup>3+</sup> ratio was regulated in a chemical precipitation process (Yao et al., 2013; Li et al., 2010; Zhang et al., 2021). However, this method has a long duration; and the synthesized precipitate needs washing several times to remove the alkali attached to its surface (Subbaiah et al., 2002).

Pan synthesized Al-substituted  $\alpha$ -Ni(OH)<sub>2</sub> from Al(NO<sub>3</sub>)<sub>2</sub>-Ni (NO<sub>3</sub>)<sub>2</sub> solution by electrodeposition (Pan et al., 2003). Zhang prepared Al-substituted  $\alpha$ -Ni(OH)<sub>2</sub> from AlCl<sub>3</sub>-NiCl<sub>2</sub> solution (Zhang et al., 2021). Compared to the chemical precipitation method, electrodeposition method takes advantages of a low cost and shorter duration. Unfortunately, the OH<sup>-</sup>/Ni<sup>2+</sup>-Al<sup>3+</sup> ratio in the reaction interface is challenging to control, making the Al content in the ending sample not efficiently managed (Zhang et al., 2021). Thus, it is clear that the preparation method of Al-substituted  $\alpha$ -Ni(OH)<sub>2</sub> still needs to be developed.

Both Al-substituted  $\alpha$ -Ni(OH)<sub>2</sub> and pure  $\alpha$ -Ni(OH)<sub>2</sub> have a layered structure stacked by Ni(OH)<sub>2</sub> layers (Li et al., 2016; Wu et al., 2021). While, the OH<sup>-</sup> in their Ni(OH)<sub>2</sub> layers is not enough, leading to the

incorporation of water molecules and anions (Cl<sup>-</sup>,  $NO_3^-$ , etc.) into the interlayer space to neutralize charges (Li et al., 2018; Zheng et al., 2017). The stability of pure  $\alpha$ -Ni(OH)<sub>2</sub> and Al-substituted  $\alpha$ -Ni(OH)<sub>2</sub> are reported ascribe to the strong electrostatic attraction between the positively charged Ni(OH)<sub>2</sub> layers and the negatively charged interlayer space (Miao et al., 2015). To further improve the stability of Al-substituted  $\alpha$ -Ni(OH)<sub>2</sub> and to enhance the stability of pure  $\alpha$ -Ni (OH)<sub>2</sub> a method was developed by introducing anions sharing enormous relative binding energy with Ni(OH)<sub>2</sub> layers to the interlayer through an ion exchange process. Maki (Maki et al., 2018) directly soaked Al-substituted  $\alpha$ -Ni(OH)<sub>2</sub> with NO<sub>3</sub><sup>-</sup> as the primary anion in the interlayer into various salt solutions and obtained Al-substituted  $\alpha$ -Ni(OH)<sub>2</sub> with related anions in the interlayer. Javashree (Javashree and Kamath, 2011) soaked pure  $\alpha$ -Ni(OH)<sub>2</sub> into saturated AlO<sub>2</sub><sup>-</sup>containing KOH solution, and found  $\alpha$ -Ni(OH)<sub>2</sub> can keep its structure by incorporation  $AlO_2^-$  from the alkaline solution.

The property of  $\alpha$ -Ni(OH)<sub>2</sub> incorporating anions from solutions encouraged us to consider whether it can incorporate cations from the solution. Suppose the feasibility of this method can be proved. Al-substituted  $\alpha$ -Ni(OH)<sub>2</sub> will be prepared by soaking pure  $\alpha$ -Ni (OH)<sub>2</sub> into the pure aluminum salt solution, and Al-substituted  $\alpha$ -Ni (OH)<sub>2</sub> with desired anions in the interlayer can be prepared by soaking pure  $\alpha$ -Ni(OH)<sub>2</sub> into the solution containing Al<sup>3+</sup> and desired anions. Al-substituted  $\alpha$ -Ni(OH)<sub>2</sub> with required Al content can be prepared by controlling the ratio of pure  $\alpha$ -Ni(OH)<sub>2</sub> soaked in the solution and Al<sup>3+</sup> dissolved in the solution, which overcomes the shortcomings of chemical precipitation (long duration times and products needing to be washed many time to remove the alkali adhered to its surface) and electrodeposition simultaneously (the Al content in the product cannot be controlled because the ratio of OH<sup>-</sup>/Al<sup>3+</sup>-Ni<sup>2+</sup> is not easy to be controlled in the process of electrodeposition).

By directly soaking pure  $\alpha\text{-Ni}(OH)_2$  into pure AlCl<sub>3</sub> and AlCl<sub>3</sub>-Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solutions, the present work attempts to prepare Alsubstituted  $\alpha\text{-Ni}(OH)_2$  and Al-substituted  $\alpha\text{-Ni}(OH)_2$  with S<sub>2</sub>O<sub>3</sub><sup>2-</sup> as the main interlayer anion.

#### 2. Experimental

#### 2.1. Reactants

The covered reactants, analytical grade  $NiCl_2 \cdot 6H_2O$ ,  $AlCl_3 \cdot 6H_2O$ ,  $Na_2S_2O_3 \cdot 5H_2O$ , and anhydrous ethanol were purchased and used directly.

# 2.2. The process of the sample preparation

As shown in Fig. 1, pure  $\alpha$ -Ni(OH)<sub>2</sub> was electrodeposited from a 0.3 M NiCl<sub>2</sub> solution in a three-chambers electrolytic cell. The cell was assembled with two side-set anodic chambers and a middle-set cathodic chamber. Chambers were separated by cation-exchange membrane. In an electrodeposition process involved in the present work, pure water and water-ethanol at a volume ratio of 1:1 separately served as the solvent for the anolyte and catholyte. The electrodeposition was conducted at a current density related to the cathode sheet of 15 mA/  $cm^2$  under room temperature with a duration of 60 min. Then, the initial sample was collected from the cathodic chamber by washing with deionized water thoroughly, filtration, drying at 60 °C in oven for constant weight, and grounded in a mortar. Further, pure  $\alpha$ -Ni(OH)<sub>2</sub> was dispersed in pure AlCl<sub>3</sub> solution and AlCl<sub>3</sub>-Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution. Then, the suspensions were transferred to a constant-temperature shaker for 8 h at 25 °C under a rotation rate of 180 r/min (TS-2102C, China). The mass of  $\alpha$ -Ni(OH)<sub>2</sub> dispersed in the Al-containing salt solution



Fig. 1 Diagram of the sample preparation process.

was 1.0 g (9.4 mmol). The molar ratios of  $\alpha$ -Ni(OH)<sub>2</sub>/AlCl<sub>3</sub> were set to 1:0.1, 1:0.2, 1:0.4 and 1:0.8. In the Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>containing solutions, the molar ratio of  $\alpha$ -Ni(OH)<sub>2</sub>/Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> was constant at 1:2. With the increasing Al content in the solutions, the pure AlCl<sub>3</sub> solutions were marked as Al-1s, Al-2s, Al-3s, and Al-4s; and the resultant samples were marked as Al-1, Al-2, Al-3, and Al-4. The AlCl<sub>3</sub>-Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solutions were marked as Al-S-1s, Al-S-2s, Al-S-3s, and Al-S-4s, and the corresponding samples were marked as Al-S-1, Al-S-2, Al-S-3, and Al-S-4. After being immersed, the collected samples were washed, filtered, dried, and grounded, as mentioned above.

The pure  $\alpha$ -Ni(OH)<sub>2</sub> was marked as Al-0. The pH of the solutions before and after immersing was recorded using acidometer (LEICI, PHS-3E, China). Due to the acidic property of the AlCl<sub>3</sub> solution and reactions of Eqs. (6) and (7), the AlCl<sub>3</sub>-Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solutions used for immersing  $\alpha$ -Ni(OH)<sub>2</sub> were filtrates of the newly prepared ones.

$$S_2O_3^{2-} + 2H^+ \to H_2S_2O_3$$
 (6)

$$H_2S_2O_3 \to SO_2 \uparrow +S \downarrow +H_2O \tag{7}$$

# 2.3. Characterization of the samples

The phase determination of the sample was performed using a Bruker D8 X-ray diffractometer (XRD), USA. The Fourier-transform infrared spectroscopy (FT-IR) of the sample was recorded on a Nicolet iS50 infrared spectrometer, USA. The Al, Ni, Cl<sup>-</sup> and  $S_2O_3^{2-}$  contents were measured using X-ray fluorescence (XRF, ZSX100e, Japan). The strong alkali solution stability of the samples was performed by immersing 200 mg of each sample in 40 mL 6 M KOH at ambient temperature. After washed and filtered, the sample soaked in strong alkali solution was collected and send to phase analysis to judge its stability.

#### 3. Results and discussion

# 3.1. Analysis of the XRD patterns

Fig. 2 shows the XRD patterns of the initial sample (pure  $\alpha$ -Ni (OH)<sub>2</sub>, Al-0) and that collected from pure AlCl<sub>3</sub> solution (Al-1 to Al-4) and AlCl<sub>3</sub>-Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution (Al-S-1 to Al-S-4). It was observed that the number and the location for the diffraction peaks on each pattern were identical, indicating all the samples had the same phase. Their diffractions setting at about 11.5°, 23°, 33°, 38.5°, and 60° was indexed as the (003), (006), (101), (015), and (110) planes for  $\alpha$ -Ni(OH)<sub>2</sub>. Except for the above-mentioned diffraction peaks, no peaks related to Al(OH)<sub>3</sub> were detected for the samples collected from pure AlCl<sub>3</sub> solution and AlCl<sub>3</sub>-Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution, indicating there was no Al(OH)<sub>3</sub> in the samples.

As shown in Fig. 2, the XRD patterns for the samples collected from pure AlCl<sub>3</sub> solution and AlCl<sub>3</sub>-Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution could not wholly coincide with the initial sample (Al-0). Meanwhile, the intensity of the characteristic peak for  $\alpha$ -Ni(OH)<sub>2</sub> at about 11.5° was notably higher for the samples collected from pure AlCl<sub>3</sub> solution than AlCl<sub>3</sub>-Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution. The above two demonstrate that some changes occurred in the lattice of the initial  $\alpha$ -Ni(OH)<sub>2</sub> during immersion.

# 3.2. Analysis of the FT-IR spectrums

The averaged long-range structure of the samples can be obtained from the XRD analysis (Ramesh and Vishnu, 2006). The short-range coordination of the samples can be obtained from the FT-IR spectrums, and FT-IR analysis was used to complete the XRD analysis (Ramesh and Vishnu, 2006; Zhang et al., 2020).  $\alpha$ -Ni(OH)<sub>2</sub> showed a hydrotalcite-like structure, and its Ni(OH)<sub>2</sub> layer was disorderedly stacked



Fig. 2 The XRD patterns of the initial sample (Al-0) and that collected from various solutions: (a) pure AlCl<sub>3</sub> solution (Al-1 to Al-4) and (b) AlCl<sub>3</sub>-Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution (Al-S-1 to Al-S-4).

(Andrade et al., 2018; Li et al., 2018). The disordered internal structure led to low intensity for its diffraction peaks (Li et al., 2018). To offer a complementary for the phase determination by the serrated-like diffraction peaks as seen in Fig. 2 and evaluate the effect of soaking on the short-range coordination of the resultant samples, the FT-IR were performed, and the results are depicted in Fig. 3.

Fig. 3a shows the comparison of the FT-IR spectrums for the Al-0 and the samples collected from pure AlCl<sub>3</sub> solution. The broad peak at about  $3460 \text{ cm}^{-1}$  corresponds to the vibration for the H-boned OH<sup>-</sup> groups. The tiny peak at about 1640 cm<sup>-1</sup> corresponds to the bending vibration for the H<sub>2</sub>O molecules, confirming the existence of interlayer H<sub>2</sub>O molecules (Li et al., 2018; Li et al., 2010; Shangguan et al., 2015). The two little waves at about 1467 and  $1380 \text{ cm}^{-1}$  could be attributed to the symmetric and asymmetric vibration of the intercalated  $CO_3^{2-}$  (Jayashree and Kamath, 2011). The peak at about 1085 cm<sup>-1</sup> was ascribed to the vibration of the intercalated Cl<sup>-</sup> (Zhang et al., 2020). The deep peak at about 618 cm<sup>-1</sup> corresponds to the vibration of the in-plane Ni-O-H (Li et al., 2010; Miao et al., 2015). It was observed from the above analysis that the FT-IR spectrums for the Al-0 and the samples obtained by directly immersing Al-0 into AlCl<sub>3</sub> solution showed the same vibrations as that of α-Ni  $(OH)_2$ . They all have a layered structure stacked by Ni $(OH)_2$ layers, and  $H_2O$  molecules,  $Cl^-$  and  $CO_3^{2-}$  were present in the layer space.

In particular, the wave between 1300 and 500 cm<sup>-1</sup> for samples Al-0 to Al-4 was selected from Fig. 3b. As seen in Fig. 3b, the intercalated Cl<sup>-</sup> vibration was found to become unremarkable from sample Al-0 to Al-4. Meanwhile, the vibration for the in-plane Ni-O-H negatively moved from Al-0 to Al-4. In the previous work, which included the preparation of Al-substituted  $\alpha$ -Ni(OH)<sub>2</sub> by electrodeposition from a NiCl<sub>2</sub>-AlCl<sub>3</sub> solution, the peak for the vibrations of the intercalated Cl<sup>-</sup> and the in-plane Ni-O-H was separately observed to turn weak and negatively move with the increasing Al content in the sample (Zhang et al., 2021). Thus, the observation in Fig. 3b indicated a rising Al content in the sample from Al-0 to Al-4.

Fig. 3c presents the FT-IR spectrums for the Al-0 and the samples collected from the AlCl<sub>3</sub>-Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution. From Fig. 3c, vibrations at about 3460, 1640, 1467, 1380, and 618 cm<sup>-1</sup> were observed on all the spectrums. However, the vibration for the intercalated Cl<sup>-</sup> in Al-0 disappeared, and two sharp vibrations appeared at about 1115 cm<sup>-1</sup> and 1105 cm<sup>-1</sup> in the FT-IR spectrums for Al-S-1 to Al-S-4, which can be ascribed to the vibration for the intercalated S<sub>2</sub>O<sub>3</sub><sup>2-</sup>. From the spectrums selected from Fig. 3d, no noticeable shift was detected for the vibration of the in-plane Ni-O-H from Al-0 to Al-S-4.

# 3.3. Analysis of the immersing process

The FT-IR analysis in Fig. 3 demonstrates that the Al-0 may have incorporated Al and  $S_2O_3^{2-}$  from the soaked solutions. To study the interaction between the Al-0 and the soaked solutions, the pH for the pure AlCl<sub>3</sub> solution and the AlCl<sub>3</sub>-Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution before and after soaking  $\alpha$ -Ni(OH)<sub>2</sub> are tabulated in the Table 1. The content for Ni, Al, Cl<sup>-</sup>, S<sub>2</sub>O<sub>3</sub><sup>-</sup> in the samples collected from pure AlCl<sub>3</sub> solution and AlCl<sub>3</sub>-Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution are recorded in Table 2.

As seen from the Table 1, the pH for pure AlCl<sub>3</sub> solution and AlCl<sub>3</sub>-Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution before and after soaking α-Ni  $(OH)_2$  was acidic due to Eq. (8). Affected by the presence of  $S_2O_3^{2-}$  in the solution, the pH of AlCl<sub>3</sub>-Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solutions was slightly higher than pure AlCl<sub>3</sub> solution before and after soaking  $\alpha$ -Ni(OH)<sub>2</sub>. Thus, after soaking  $\alpha$ -Ni(OH)<sub>2</sub>, the pH for each solution slightly increased, suggesting the occurrence of Eq. (9) during soaking. The event of Eq. (9) was also proved from Fig. 4. Fig. 4 shows the images for pure water and the filtrates for AlCl<sub>3</sub> solution and AlCl<sub>3</sub>-Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution after soaking  $\alpha$ -Ni(OH)<sub>2</sub>. As seen from Fig. 4, the filtrates for AlCl<sub>3</sub> solution and  $Na_2S_2O_3$  solution after soaking  $\alpha$ -Ni(OH)<sub>2</sub> were light green, demonstrating the presence of Ni<sup>2+</sup> in the solutions. The filtrate for pure AlCl<sub>3</sub> solution after soaking  $\alpha$ -Ni (OH)<sub>2</sub> was greener than AlCl<sub>3</sub>-Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution, indicating more  $\alpha$ -Ni(OH)<sub>2</sub> was dissolved in pure AlCl<sub>3</sub> solution.



Fig. 3 Comparison of the FT-IR spectrums between the Al-0 and the samples collected from the Al-containing salt solutios: (a)-(b) pure AlCl<sub>3</sub> solution, and (c)-(d) AlCl<sub>3</sub>-Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution.

$$Al^{3+} + 3H_2O \rightleftharpoons Al(OH)_3 \downarrow + 3H^+$$
(8)

$$\alpha - \operatorname{Ni}(\operatorname{OH})_2 + 2\operatorname{H}^+ \to \operatorname{Ni}^{2+} + 2\operatorname{H}_2\operatorname{O}$$
(9)

As shown in the Table. 2, Al was detected in the samples collected from pure AlCl<sub>3</sub> solution and AlCl<sub>3</sub>-Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution. While no diffraction peaks related to Al(OH)<sub>3</sub> were observed from the XRD analysis in Fig. 2, and no vibration corresponded to Al-O-H was detected from the FT-IR analysis. The above results demonstrated that Al was inserted into the lattice of Al-0 during the immersion process. Thus, Al-substituted  $\alpha$ -Ni(OH)<sub>2</sub> was successfully prepared by immersing pure  $\alpha$ -Ni(OH)<sub>2</sub> in Al-containing salt solution directly (Shangguan et al., 2015; Miao et al., 2015).

According to the above analysis, the reaction that took place during immersing was conducted as follows:

(I) When immersing  $\alpha$ -Ni(OH)<sub>2</sub> in both AlCl<sub>3</sub> solution and AlCl<sub>3</sub>-Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution, the reaction shown in Eq. (9) occurred on the surface of pure  $\alpha$ -Ni(OH)<sub>2</sub> particles. Then,

 $Ni^{2+}$  was present near the surface of pure  $\alpha$ -Ni(OH)<sub>2</sub> particles as shown in Fig. 5a.

$$\alpha - \operatorname{Ni}(\operatorname{OH})_2 + 2\operatorname{H}^+ \to \operatorname{Ni}^{2+} + 2\operatorname{H}_2\operatorname{O}$$
(9)

(II) As shown in Fig. 5b, with Eq. (9) proceeding, the Ni<sup>2+</sup> concentration increased, and the H<sup>+</sup> concentration decreased near the surface of pure  $\alpha$ -Ni(OH)<sub>2</sub> particles. Thus, the OH<sup>-</sup> near the surface of the  $\alpha$ -Ni(OH)<sub>2</sub> particles became free with the decreasing concentration of H<sup>+</sup>. Next, Ni<sup>2+</sup>, Al<sup>3+</sup>, and OH<sup>-</sup> were present near the surface of the  $\alpha$ -Ni(OH)<sub>2</sub> particles. Meanwhile, Eq. (8) right moved, and Eq. (3) occurred followed by Eq. (5).

$$Al^{3+} + 3H_2O \rightleftharpoons Al(OH)_3 \downarrow + 3H^+$$
(8)

$$Al^{3+} + 3OH^{-} \rightleftharpoons Al(OH)_{3} \tag{3}$$

$$Al(OH)_3 + OH^- \rightleftharpoons AlO_2^- + 2H_2O$$
<sup>(5)</sup>

Table 1	pH for both pure AlCl <sub>3</sub> solutions and AlCl <sub>3</sub> -Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> solutions before (Initial) and after (Ending) soaking $\alpha$ -Ni(OH) <sub>2</sub> .							
	Al-1S	Al-2S	Al-3S	Al-4S	Al-S-1S	Al-S-2S	Al-S-3S	Al-S-4S
Initial pH Ending p	4.30 H 4.82	4.21 4.39	4.09 4.17	3.95 4.02	4.41 4.91	4.29 4.45	4.13 4.20	3.99 4.11

<b>Tuble 2</b> The content of Tay, in, or and by 0, in each bampies (mor	Table 2	The content	of Ni, Al,	, Cl <sup>-</sup>	and $S_2O_3^2$	in	each	samples	(mol	).
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	Al-0	Al-1	A1-2	A1-3	Al-4	Al-S-1	Al-S-2	Al-S-3	Al-S-4
Ni	1.201	1.119	1.098	1.056	0.973	1.083	1.073	0.998	0.971
Al	0	0.043	0.089	0.159	0.211	0.0404	0.071	0.173	0.225
Cl	0.141	0.122	0.113	0.113	0.102	0.016	0.020	0.022	0.025
$S_2O_3^{2-}$	-	-	-	-	-	0.101	0.118	0.139	0.151



Fig. 4 Images for pure water and filtrates for both pure AlCl<sub>3</sub> solution and AlCl<sub>3</sub>-Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution after soaking α-Ni(OH)<sub>2</sub>.



Fig. 5 Schematic diagram for the chemical reaction in immersing process.



(III) The synergetic effect of Eqs. (5), (8), and (9) increased the OH<sup>-</sup> concentration near the surface of  $\alpha$ -Ni(OH)<sub>2</sub> particles. When the concentration of the OH<sup>-</sup>, Al<sup>3+</sup> and Ni<sup>2+</sup> reached the required concentration for precipitating Alsubstituted  $\alpha$ -Ni(OH)<sub>2</sub> (Eq.4), the Al-substituted  $\alpha$ -Ni(OH)<sub>2</sub> started to form as shown in Fig. 5c.

$$Al(OH)_3 + OH^- \rightarrow AlO_2^- + 2H_2O$$
<sup>(5)</sup>

$$Al^{3+} + 3H_2O \rightleftharpoons Al(OH)_3 \downarrow + 3H^+$$
(8)

Notably, the concentrations of OH<sup>-</sup>, Al<sup>3+,</sup> and Ni<sup>2+</sup> required for precipitation of Al-substituted  $\alpha$ -Ni(OH)<sub>2</sub> with different Al content were different. Thus, the Al content in the Al-substituted  $\alpha$ -Ni(OH)<sub>2</sub> was affected not only by the ratio of Ni<sup>2+</sup>/Al<sup>3+</sup> in the solution but also by the pH of the solution. As seen from the Table. 2, for the solutions with the same initial Al content, the Al content in the corresponding samples collected from pure AlCl<sub>3</sub> solution was slightly higher than AlCl<sub>3</sub>-Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution, which was attributed to the effect of S<sub>2</sub>O<sub>3<sup>-</sup></sub> in the solution on pH and the reaction rate for Eqs. (4) and (9). The Al content in the samples collected from pure AlCl<sub>3</sub>-Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution was increased with the increasing Al content in the initial soaking solutions.

After that, the Cl<sup>-</sup> content in the sample collected from the pure AlCl<sub>3</sub> solution was decreased from Al-0 to Al-4, which was proved by the weakening vibration for intercalated Cl<sup>-</sup> on the corresponding FT-IR spectrums, as shown in Fig. 3b. For the samples collected from AlCl<sub>3</sub>-Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solutions, their Cl<sup>-</sup> content was much lower than pure AlCl<sub>3</sub> solution. However, their  $S_2O_3^{2-}$  content was higher than Cl<sup>-</sup> content, which demonstrated that the mainly intercalated anion in the Alsubstituted  $\alpha$ -Ni(OH)<sub>2</sub> collected from AlCl<sub>3</sub>-Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution was  $S_2O_3^{2-}$ . Herein,  $S_2O_3^{2-}$  entered the interlayer through Eq. (4) or through ion exchange with the intercalated  $Cl^{-}$ . The  $Cl^{-}$  content and the  $S_2O_3^{2-}$  content was increased from Al-0 to Al-S-4. This is mainly because the positive charges in the Ni(OH)<sub>2</sub> layers increase with the increase of Ni atoms substituted by Al atoms, and the negative charges that need to be taken in the interlayers to compensate these positive charges should also increase (Miao et al., 2015).

# 3.4. Analysis of the stability in strongly alkaline solution

Fig. 6 shows the XRD patterns for various samples before and after soaking in 6 M KOH. For the Al-0, the diffraction peaks corresponding to  $\alpha$ -Ni(OH)<sub>2</sub> disappeared after 1-day soaking in 6 M KOH, suggesting that the conversion between the initial  $\alpha$ -Ni(OH)<sub>2</sub> and  $\beta$ -Ni(OH)<sub>2</sub> was completed. On prolonged soaking in 6 M KOH, the diffraction peaks related to  $\beta$ -Ni (OH)<sub>2</sub> were sharpened.

As seen from Fig. 6b and c, after 1-day soaking the samples Al-1, Al-2, Al-S-1, and Al-S-2 in 6 M KOH, the diffraction

peaks belonging to  $\alpha$ -Ni(OH)<sub>2</sub> at about 11.5° weakened, while the peak at about 23° moved left towards the diffraction peak for  $\beta$ -Ni(OH)<sub>2</sub> at about 19°. Further, the diffraction peaks at about 33° and 38° were completely transformed into that for  $\beta$ -Ni(OH)<sub>2</sub> at a similar position, and at about 60°, it was split into two peaks corresponding to  $\beta$ -Ni(OH)<sub>2</sub> at bout 59° and 62.5°. Meanwhile, new peaks at about 52°, 69.5° and 72.5° related to  $\beta$ -Ni(OH)<sub>2</sub> appeared at the XRD patterns for Al-1, Al-2, Al-S-1, and Al-S-2 after 1-day soaking in 6 M KOH. Moreover, extending the soaking time to 5 days, the peak represented  $\alpha$ -Ni(OH)<sub>2</sub> at about 11.5° further weakened, and the peaks for  $\beta$ -Ni(OH)<sub>2</sub> at about 69.5° and 72.5° was strengthened.

For the samples Al-3, Al-4, Al-S-3 and Al-S-4, after 1-day soaking in 6 M KOH solution, the diffraction peaks belonging to  $\alpha$ -Ni(OH)<sub>2</sub> at about 11.5° sharpened, at about 23° split into a very weak peak at same position and a peak between 23° for  $\alpha$ -Ni(OH)<sub>2</sub> and 19° for  $\beta$ -Ni(OH)<sub>2</sub>, at about 33° split into a tiny peak at identical position and a sharp peak corresponding to  $\beta$ -Ni(OH)<sub>2</sub>, at about 38° almost completely converted to the diffraction peak related to  $\beta$ -Ni(OH)<sub>2</sub> at silimar position, and at about 60° split into two peaks corresponding to  $\alpha$ -Ni(OH)<sub>2</sub> at bout 59.9° and 61.2°. Further extending the soaking time to 5 days, two peaks for  $\beta$ -Ni(OH)<sub>2</sub> at about 69.5° and 72.5° appeared at the XRD patterns for Al-3, Al-4, Al-S-3, and Al-S-4.

After being soaked simultaneously, the intensity of the existing characteristic peak for  $\alpha$ -Ni(OH)<sub>2</sub> at about 11.5° increased. The sawtooth shape of the diffraction peak became more and more evident from Al-1 to Al-4 and from Al-S-1 to Al-S-4, indicating more components for  $\alpha$ -Ni(OH)<sub>2</sub> reserved from Al-1 to Al-4 and from Al-S-1 to Al-S-4.

Fig. 6d presents the XRD patterns for three samples with similar Al content after immersing in KOH solution for five days. The samples prepared using electrodeposition from an AlCl<sub>3</sub>-NiCl<sub>2</sub> solution (Al-E) were found to have the most diffraction peaks belonging to  $\alpha$ -Ni(OH)<sub>2</sub>; the components for  $\alpha$ -Ni(OH)<sub>2</sub> reserved on the XRD patterns for Al-4 and Al-S-4 were comparable. Thus, Al-E showed the highest stability, and the stability of Al-4 and Al-S-4 needs to be improved.

The above analysis demonstrated that a preliminary stabilized Al-substituted  $\alpha$ -Ni(OH)<sub>2</sub> was obtained by directly soaking the pure  $\alpha$ -Ni(OH)<sub>2</sub> in pure AlCl<sub>3</sub> and AlCl<sub>3</sub>-Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution.

#### 4. Conclusions

In the present study, Al-substituted  $\alpha$ -Ni(OH)<sub>2</sub> was prepared directly by soaking pure  $\alpha$ -Ni(OH)<sub>2</sub> into AlCl<sub>3</sub> solution. The S<sub>2</sub>O<sub>3</sub><sup>2-</sup> was introduced into AlCl<sub>3</sub> solution, where Al-substituted  $\alpha$ -Ni(OH)<sub>2</sub> with S<sub>2</sub>O<sub>3</sub><sup>2-</sup> was obtained as the primary anion in the interlayer. By adjusting the ratio of pure  $\alpha$ -Ni(OH)<sub>2</sub> soaked in the solution and Al<sup>3+</sup> dissolved in the solution, Al-substituted  $\alpha$ -Ni(OH)<sub>2</sub> with different Al content was synthesized. The Al element entered the lattice of pure  $\alpha$ -Ni

Fig. 6 XRD patterns for samples before and after being immersed in 6 M KOH: (a) initial  $\alpha$ -Ni(OH)<sub>2</sub> (Al-0), (b) samples collected from AlCl<sub>3</sub>-Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution; and (d) the XRD comparison for the samples Al-4, Al-S-4 and the sample sharing similar Al content with Al-4 & Al-S-4 prepared by electrodeposition from a AlCl<sub>3</sub>-NiCl<sub>2</sub> solution (Al-E) after 5-days soaking.

(OH)<sub>2</sub> through a process, where pure  $\alpha$ -Ni(OH)<sub>2</sub> was dissolved followed by the precipitation of Al<sup>3+</sup>, Ni<sup>2+</sup> and OH<sup>-</sup>. The S<sub>2</sub>O<sub>3</sub><sup>2-</sup> entered the interlayer of Al-substituted  $\alpha$ -Ni(OH)<sub>2</sub> through the formation process of the Al-substituted  $\alpha$ -Ni(OH)<sub>2</sub> or though ion exchange with the intercalated Cl<sup>-</sup>. The Al-substituted  $\alpha$ -Ni(OH)<sub>2</sub> prepared by soaking pure  $\alpha$ -Ni(OH)<sub>2</sub> into AlCl<sub>3</sub>-containing solutions obtained preliminary stability in the strongly alkaline solution.

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#### References

- Andrade, T.M., Danczuk, M., Anaissi, F.J., 2018. Effect of precipitating agents on the structural, morphological, and colorimetric characteristic of nickel hydroxide particles. Colloid Interfac Sci. 23, 6–13.
- Ash, B., Khetic, K., Subbaiaah, T., Anand, S., Paramguru, R.K., 2006. Physcio-chemical and electro-chemical properties of nickel hydroxide precipitated in the presence of metal additives. Hydrometallurgy 84, 250–255.
- Bao, J., Zhu, Y.J., Zhuang, Y.H., Xu, Q.S., Zhao, R.D., Liu, Y.L., Zhong, H.L., 2013. Structure and electrochemical performance of Cu singly doped and Cu/Al co-doped nano-nickel hydroxide. Trans. Nonferrous Met. Soc. China 23, 445–450.
- Chen, H., Wang, J.M., Pan, T., Xiao, H.M., Zhang, J.Q., Cao, C.N., 2002. Effects of coprecipitated zinc on the structure and electrochemical performance of Ni/Al-layered double hydroxide. Int. J. Hydroge. Energ. 27, 489–496.
- Fang, K.L., Chen, M.F., Chen, J.Z., Tian, Q.H., Wong, C.P., 2019. Cotton stalk-derived carbon fiber@Ni-Al layered double hydroxide nanosheets with improved performances for supercapacitors. Appl. Surf. Sci. 475, 372–379.
- Gao, T., Jelle, B.P., 2013. Paraotwayite-type α-Ni(OH)<sub>2</sub> nanowires: structural, optical and electrochemical properties. J. Phys. Chem. C 117 (33), 17294–17302.
- Gualandi, I., Monti, M., Scavetta, E., Tonelli, D., Prevot, V., Mousty, C., 2015. Electrodeposition of layered double hydroxides on platinum: Insights into the reactions sequence. Electrochim. Acta 152, 75–83.
- Hu, M., Yang, Z.Y., Lei, L.X., Sun, Y.M., 2011. Structural transformation and its effects on the electrochemical performances of a layered double hydroxide. J. Power Sources 196, 1569–1577.
- Huang, H.L., Guo, Y.J., Cheng, Y.H., 2018. Ultrastable α phase nickel hydroxide as energy storage materials for alkaline secondary batteries. Appl. Surf. Sci. 435, 635–640.
- Jayashree, R.S., Kamath, P.V., 2011. Suppression of the α→β-nickel hydroxide transformation in concentrated alkali: Role of dissolved cations. J. Appl. Electrochem. 31, 1315–1320.
- Jayashree, R.S., Vishnu, K.P., 2001. Nickel hydroxide electrodeposition from nickel nitrate solutions: mechanistic studies. J. Power Sources 93, 273–278.
- Li, J.L., Aslam, M.K., Chen, C.G., 2018. One-pot hydrothermal synthesis of porous  $\alpha$ -Ni(OH)<sub>2</sub>/C composites and its application in Ni/Zn alkaline rechargeable battery. J. Electrochem. Soc. 165 (5), A910–A917.
- Li, J.L., Aslam, M.K., Chen, C.G., 2018. One-pot hydrothermal synthesis of porous  $\alpha$ -Ni(OH)<sub>2</sub>/C composites and its application in Ni/Zn alkaline rechargeable battery. J. Electrochem. Soc. 165, A910–A917.
- Li, H., Ma, J., Evans, D.G., Zhou, T., Li, F., Duan, X., 2016. Molecular dynamics modeling of the structures and binding energies of α-nickel hydroxides and nickel-aluminum layered

double hydroxides containing various interlayer guest anions. Chem. Mater. 18, 4405–4414.

- Li, Y.W., Yao, J.H., Liu, C.J., Zhao, W.M., Deng, W.X., Zhong, S.K., 2010. Effect of interlayer anions on the electrochemical performance of Al-substituted α-type nickel hydroxide electrodes. Int. J. Hydroge. Energ. 35, 2539–2545.
- Maki, H., Inoue, M., Mizuhata, M., 2018. Charge transfer resistance reduction by the interlayer distance expansion of Ni-Al layered double for nickel-metal hydride battery anode. Electrochim. Acta 270, 395–401.
- Miao, C.C., Zhu, Y.J., Huang, L.G., Zhao, T.Q., 2015. The relationship between structural stability and electrochemical performance of multi-element doped alpha nickel hydroxide. J. Power Sources 274, 186–193.
- Nai, J.W., Chen, Z.B., Li, H.P., Li, F.Y., Bai, Y., Li, L.D., Guo, L., 2013. Structure-dependent electrocatalysis of Ni(OH)<sub>2</sub> hourglasslike nanostructures towards L-histidine. Chem. Eur. J. 19, 501–508.
- Nethravathi, C., Ravishankar, N., Shivakumara, C., Rajamathi, M., 2007. Nanocomposites of  $\alpha$ -hydroxides of nickel cobalt by delamination and co-stacking: enhanced stability of  $\alpha$ -motifs in alkaline medium and electrochemical behavior. J. Power Sources 172, 970–974.
- Ortiz, M.G., Castro, E.B., Real, S.G., 2014. Effect of cobalt electrodes deposition on nickel hydroxide electrodes. Int. J. Hydrogen Energ. 39, 6006–6012.
- Pan, T., Wang, J.M., Zhao, Y.L., Chen, H., Xiao, H.M., Zhang, J.Q., 2003. Al-stabilized α-nickel hydroxide prepared by electrochemical impregnation. Mater. Chem. Phys. 78, 711–718.
- Ramesh, T.N., Vishnu, K.P., 2006. Synthesis of nickel hydroxide: Effect of precipitation conditions on phase selectivity and structural disorder. J. Power Sources 156, 655–661.
- Shangguan, E.B., Li, J., Guo, D., Guo, L.T., Nie, M.Z., Chang, Z.R., Yuan, X.Z., Wang, H.J., 2015. A comparative study of structural and electrochemical properties of high-density aluminum substituted α-nickel hydroxide containing different interlayer anions. J. Power Sources 282, 158–168.
- Subbaiah, T., Mallic, S.C., Mishra, K.G., Sanjay, K., Das, R.P., 2002. Electrochemical precipitation of nickel hydroxide. J. Power Sources 112, 562–569.
- Wang, L.Q., Li, X.C., Guo, T.M., Yan, X.B., Tay, B.K., 2014. Threedimensional Ni(OH)<sub>2</sub> nanoflakes/graphene/nickel foam electrode with high rate capability for supercapacitor applications. Int. J. Hydrogen Energ 39, 7876–7884.
- Wu, D., Shen, X.Y., Liu, X.K., Liu, T., Luo, Q.Q., Liu, D., Chen, T., Wang, L., Cao, L.L., Yao, T., 2021. Insight into Fe activating onedimensional α-Ni(OH)<sub>2</sub> nanobelts for efficient oxygen evolution reaction. J. Phys. Chem. C 125, 20301–20308.
- Yao, J.H., Li, Y.W., Li, Y.X., Zhu, Y.X., Wang, H.B., 2013. Enhanced cycling performance of Al-substituted  $\alpha$ -nickel hydroxide by coating with  $\beta$ -nickel hydroxide. J. Power Sources 224, 236– 240.
- Zhang, Z.G., Huo, H., Yu, Z.J., Xiang, L.Z., Xie, B.X., Du, C.Y., Wang, J.J., Yin, G.P., 2021. Unraveling the reaction mechanism of low dose Mn dopant in Ni(OH)<sub>2</sub> supercapacitor electrode. J. Energy Chem. 61, 497–506.
- Zhang, J.J., Zhang, T.A., Feng, S., 2020. α-Ni(OH)<sub>2</sub> electrodeposition from NiCl<sub>2</sub> solution. Trans. Nonferrous Met. Soc. China 30, 2802– 2811.
- Zhang, J.J., Zhang, T.A., Feng, S., 2021. Ni-Al layered double hydroxides electrodeposition from a chloride solution. Arab. J. Chem. 14, 103208.
- Zheng, Y., Zhu, B., Chen, H., You, W., Jiang, C., Yu, J., 2017. Hierarchical flower-like nickel(II) oxide microspheres with high adsorption capacity of Congo red in water. J. Colloid Interface Sci. 504, 688–696.