Novel layered double hydroxide precursor derived high-Co_9S_8-content composite as anode for lithium-ion batteries

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ABSTRACT

Layered double hydroxides (LDHs), also known as brucite ($Mg(OH)_2$)-like anionic clay compounds, are very convenient precursors with a unique flexibility of tuning component type and molar ratio toward composite nanomaterials in energy storage, such as lithium-ion batteries (LIBs). Conventional binary LDH precursors are typically converted to active/non-active transition-metal oxide composites as anode nanomaterials for LIBs, but either with the aid of additionally introducing highly conductive carbonaceous matrix, or possessing relatively high-content non-active components that greatly lower the reversible specific capacity. Herein, we demonstrate a rational design of a novel single-source precursor of dodecyl sulfonate-intercalated $Co^{2+}Co^{3+}Al^{3+}$-layered double hydroxide ($Co^{2+}Co^{3+}Al^{3+}$-LDH) and its conversion to high-Co_9S_8-content composite (Co_9S_8/S-doped carbon/Al_2O_3) as high-efficiency anode nanomaterials for LIBs. *In-situ* X-ray diffraction (XRD) reveals the controllable topotactic transformation via tuning calcination temperature and time. Electrochemical test shows that the composite electrode delivers a reversible capacity of 970 mA h g^{-1} after 200 cycles at 100 mA g^{-1}, and in particular, a long-term cycling stability of 780 mA h g^{-1} after 500 cycles at 1 A g^{-1}, manifesting highly enhanced electrochemical performances compared with the counterpart derived from a conventional binary LDH precursor. Monitoring the discharged/charged states by *in-situ* XRD and *ex-situ* Raman spectra provides a direct support to the enhancement. Our results show that the LDH precursor-based approach provides an alternative to prepare diverse transition metal sulfides for energy storage.

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1. Introduction

Layered double hydroxides (LDHs), also well-known as huge family of anionic clay compounds possessing structures based on brucite ($Mg(OH)_2$)-like layers, have stirred extensive interest in energy storage and conversion [1–6], especially including rechargeable secondary batteries, supercapacitors, and full cells. LDHs possess the general chemical formula of $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}(A^{n-})_{x/n} \cdot yH_2O$, where M^{2+} (such as Mg^{2+}, Zn^{2+}, Co^{2+} and Ni^{2+}) and M^{3+} (such as Al^{3+} and Fe^{3+}) present tunable cations occupied well-orderedly within a LDH layer, A^{n-} means an anion (such as CO_3^{2-}, NO_3^-, and surfactant anion) intercalated between LDH interlayer galleries, and x is $M^{3+}/(M^{2+} + M^{3+})$ molar ratio [7]. By virtue of the unique flexibility of easily tailoring types of cations and intercalated anions, as well as cationic molar ratios over a wide range, LDHs have been investigated intensively as very tunable precursors to prepare anode nanomaterials for lithium-ion batteries (LIBs).

Various LDH precursors were subjected directly to thermal decomposition to prepare transition-metal oxides used as anode nanomaterials for LIBs, in the main form of conventional active/ nonactive or bi-component-active binary LDH precursors [8–12]. The LDH precursors involved ZnAl-LDH nanoarrays used to synthesize $ZnO/ZnAl_2O_4$ [9], nanoparticle-like ZnFe-LDH to yield $ZnO/ZnFe_2O_4$ [10], and CoFe-LDH precursor to form $CoO/CoFe_2O_4$ nanoparticles [11], as well as MgZnFe-LDH to generate $ZnFe_2O_4/MgFe_2O_4/MgO$ [12]. To alleviate their problems of rapid capacity fading and poor cycling stability, introducing carbonaceous support (such as carbon nanotube (CNT) and graphene (G)) is one common improvement strategy [13–16]. The LDH/carbon composites mainly included $Co^{2+}Fe^{2+}Fe^{3+}$-LDH/CNT to form $CoFe_2O_4$/CNTs [14], $Co^{2+}Fe^{3+}$-LDH/G to prepare $CoO/CoFe_2O_4$/G [15], and NiAl-LDH/ glucose mixture to synthesize $Ni@NiO/Al_2O_3$/C [16]. Recently, via hydrothermal synthesis-assisted sulfuration, three-dimensional graphene aerogel supported NiCo-LDH precursor was derived to

NiCo$_2$S$_4$/Ni$_{0.96}$S composite as anode nanomaterials for LIBs [17]. All the LDH-derived transition-metal oxides and sulfides indeed exhibited their greatly enhanced electrochemical performances. However, most of the enhancements were achieved with the aid of additionally introducing highly conductive carbonaceous matrix.

Alternatively, introduction of non-active components (such as Al$_2$O$_3$) into composites is one effective approach to boost cycling stability and rate capability. The non-active component has been demonstrated to play an important role in effectively buffering volume changes of the electrochemically actives and preventing aggregation of the active nanoparticles during the cycles [18]. Typically, the strategy were employed to cathode or anode nanomaterials for LIBs, either mainly by coating several-nanometer-thick ultrathin Al$_2$O$_3$ using an advanced atomic layer deposition (ALD) technique [19], by elaborately controlled wet-chemical method [20,21], or by incorporating Al$_2$O$_3$ and the active via a high-energy mechanical milling [22]. Similarly, for the Al-containing LDH precursors derived multiple-component electrode composites [16,23,24], the formation of Al$_2$O$_3$ indeed greatly enhanced cycling stability and rate capability of the resulting composites. However, the enhancement compromised at the cost of remarkably lowering the reversible capacities. Therefore, it is a challenge to directly convert conventional Al-containing LDH precursors to composites possessing high-content active component and low-content non-active Al$_2$O$_3$ when combining non-active Al$_2$O$_3$ and carbonaceous matrix for synergistic lithium storage, because of the intrinsic feature of possessing a relatively high-content non-active components that greatly lower the specific capacity.

Herein, we report a rational design of a novel single-source precursor of dodecyl sulfonate (DS$^-$)-intercalated Co^{2+}Co^{3+}Al^{3+}-layered double hydroxide (Co^{2+}Co^{3+}Al^{3+}-DS$^-$-LDH) and its conversion to high-Co$_9$S$_8$-content Co$_9$S$_8$/S-doped carbon/Al$_2$O$_3$ composite (Co$_9$S$_8$/S-C/Al$_2$O$_3$) used as anode nanomaterials for LIBs (Fig. 1). In distinct contrast to a conventional binary Co^{2+}Al^{3+}-LDH with a relatively low Co^{2+}/Al^{3+} molar ratio typically ranging between 2: 1 and 4: 1, the unique Co^{2+}Co^{3+}Al^{3+}-DS$^-$-LDH precursor is rationally designed to contain a remarkably high molar-ratio Co/Al (8.6: 1), and well-intercalated DS$^-$ anions confined between the LDH interlayer galleries. The novel ternary LDH precursor is converted to the Co$_9$S$_8$/S-C/Al$_2$O$_3$ composite with the following advantages of improving the electrochemical performances: (i) the high-content Co component capable of forming high-content electrochemically active Co$_9$S$_8$ that can contribute to specific capacity; (ii) the intercalated DS$^-$ anion as dual molecular S and C sources transformed to the conductive S-doped carbon coating; and (iii) low-content Al component to form non-active Al$_2$O$_3$ matrix that facilitates cycling stability. *In-situ* XRD characterization reveals the topotactic conversion of the LDH precursor. The electrochemical tests show that the Co$_9$S$_8$/S-C/Al$_2$O$_3$ electrode delivers the excellent electrochemical performances for lithium-ion battery,

which were supported by monitoring the discharge/charge process using *in-situ* XRD and *ex-situ* Raman spectroscopy.

2. Experimental section

2.1. Preparation of Co^{2+}Co^{3+}Al^{3+}-DS$^-$-LDH precursor

Nanosized Co^{2+}Co^{3+}Al^{3+}-DS$^-$-LDH precursor was prepared via a modified conventional precipitation method. Briefly, a mixture of Co(NO$_3$)$_2$·6H$_2$O (18 mmol), Al(NO$_3$)$_3$·9H$_2$O (2 mmol), H$_2$O$_2$ (1 mL) and SDS (10 mmol) was dissolved in 100 mL of deionized and decarbonated water, then titrated by adding a basic solution of NaOH (100 mmol, 100 mL) with strongly stirring under N$_2$ atmosphere for 40 min to form a deep green solution at room temperature until pH = 10.5. The slurry was then transferred into a Teflon-lined stainless steel autoclave with a capacity of 200 mL. The autoclave was sealed and maintained at 120 °C for 24 h. The Co^{2+}Co^{3+}Al^{3+}-DS$^-$-LDH precursor was obtained by resining with distilled water and ethanol several times, and during at 80 °C for 24 h in a vacuum oven.

2.2. Preparation of Co$_9$S$_8$/S-C/Al$_2$O$_3$

The Co^{2+}Co^{3+}Al^{3+}-DS$^-$-LDH precursor was heated at 700 °C with a ramping rate of 5 °C min^{-1} and kept for 2 h under an Ar atmosphere. The above-obtained product (0.3 g) and thioacetamide (TAA, 4 mmol) were used as starting material, and added into 50 ml ethanol under strongly stirring. The mixture was then transferred into a Teflon-lined stainless steel autoclave, and maintained at 160 °C for 24 h. The Co$_9$S$_8$/S-C/Al$_2$O$_3$ composite was obtained by resining with distilled water and ethanol several times, and during in a vacuum oven at 60 °C for 12 h.

To highlight the contribution of the novel high-Co-content Co^{2+}Co^{3+}Al^{3+}-DS$^-$-LDH precursor, a conventional binary Co^{2+}Al^{3+}-DS$^-$-LDH precursor was prepared to yield Co$_9$S$_8$/Co/S-C/Al$_2$O$_3$ with a low-content Co$_9$S$_8$. The Co/Co$_9$S$_8$/S-C/Al$_2$O$_3$ was prepared from Co^{2+}Al^{3+}-DS$^-$-LDH under the same experimental conditions, except for a different Co^{2+}/Al^{3+} molar ratio of 3: 1, without the oxidation of H$_2$O$_2$, and no further sulfurization of TAA.

2.3. Material characterization

Powder XRD measurements were carried out by using a Rigaku XRD-6000 diffractometer (Cu Kα, 40 kV, 30 mA, λ = 0.1542 nm) over the 2θ range between 3 and 70°. The morphology of the nanocomposites was visualized by using a scanning electron microscope (SEM, ZEISS Supra 55) at an accelerating voltage of 20 kV. Transmission electron microscopy (TEM) characterization was conducted through a JEOL JEM-2100F electron microscope with an accelerating voltage of 200 kV. A confocal Raman spectrometer (Renishaw RM2000) was used to record Raman spectroscopy,
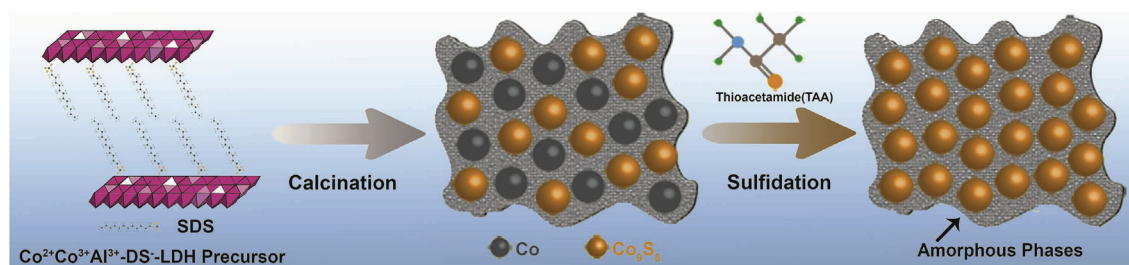

Fig. 1. Schematic illustration of preparing Co$_9$S$_8$/S-C/Al$_2$O$_3$ composite derived from a Co^{2+}Co^{3+}Al^{3+}-DS$^-$-LDH single-source precursor.