NiCo₂S₄-Based Materials for Electrochemical Applications

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NiCo₂S₄ has attracted worldwide attention in the field of energy storage/conversion. In this paper, we summarize the up-to-date progress on the preparation strategies, the applications as electrode materials for supercapacitors, lithium-ion batteries and dye sensitized solar cells, as well as electrocatalysts for the hydrogen evolution reaction, oxygen reduction reaction and oxygen evolution reaction. We also discuss the strategies to improve the electrochemical performance, and future trends of the NiCo₂S₄-based materials.

Keywords NiCo₂S₄, energy storage, preparation

Introduction

In the past decades, the issue of environment pollution and energy crisis makes the research of renewable, green energy to be a hot topic. The energy includes wind energy, solar energy, hydrogen energy, biomass-based energy, *etc.* For better applications of such energy, it is necessary to develop the technologies and equipments concerning on energy storage and conversion, for example, supercapacitors (SCs), lithium-ion batteries (LIBs), metal-air batteries, and fuel-cells. The electrode materials or electrode catalysts are crucial for the above energy devices, and their performances are largely determined by the materials. Therefore, much attention has been paid on the rational design and preparation of electrode materials or electrode catalysts with excellent properties and activities.

Figure 1 The papers on NiCo₂S₄ published in recent 5 years (until September in 2017).

NiCo₂S₄ is a typical representation of the functional materials used for energy application, and it has been heavily studied across many fields.^[1] We have used “NiCo₂S₄” as a key word, and searched the paper published in Web of Science (until September in 2017). Figure 1 shows that the research on NiCo₂S₄ has a blowout growth. The wide attention and application is related with its inherent advantages and special physical-chemical properties. NiCo₂S₄ has a thios-

pinel structure with Ni and Co occupying tetrahedral sites and octahedral sites, respectively.^[2] It is speculated that the outstanding electrochemical activity is related with the following facts: metallic conductivity ($1.25 \times 10^6 \text{ s} \cdot \text{m}^{-1}$), good redox chemistry, rich in composition and morphology.

Till date, NiCo₂S₄ with various morphology and architectures has been reported and widely used in the area of SCs, LIBs, metal-air batteries, and fuel-cells. Herein, we make a brief review and discussion on the preparation, application, and the strategies to enhance the activity of NiCo₂S₄. We also discuss the future challenges and perspectives of the NiCo₂S₄ materials.

Synthetic strategies for NiCo₂S₄

Generally, to prepare NiCo₂S₄ materials, there are three kind of routes: one-step, two-step and three step routes. The one-step method is easy by the reaction among Ni²⁺, Co²⁺ and different sulfur.^[3-5] Sometimes, impurities such as Co₉S₈ could be introduced.^[6] To avoid the impurities, it is better to use relatively higher hydrothermal temperature and longer reaction time. The one-step method usually involves with the hydrothermal process. However, there are also electrodeposited method reported.^[7-9]

Most of the publications on NiCo₂S₄ involve with the two-step procedure: formation of NiCo₂(OH)_{6-2x}(CO₃)_x ($0 \leq x \leq 1$) by Ni²⁺, Co²⁺ and different alkali (OH⁻, NH₃·H₂O, NH₄F, urea, organic base such as hexamethylenetetramine), then converting it into NiCo₂S₄ by ion-exchange reaction using different S sources such as Na₂S, NaHS, S, H₂S or organic sulfur (thiourea, thiosemicarbazide).^[11,10-12] Most of the first and second steps are usually via the hydrothermal process. The two-way method is complicated. However, using this method, we can tune the morphology of NiCo₂(OH)_{6-2x}(CO₃)_x by different salt of Ni and Co (Cl⁻, NO₃⁻, AC⁻, SO₄²⁻), alkali, reaction solvent, hydrothermal time/temperature, template (surfactant), then the shape can be maintained during the second ion-exchange process, resulting in the rational design of morphology-controlling NiCo₂S₄.

The three-step route is: formation of NiCo₂(OH)_{6-2x}(CO₃)_x ($0 \leq x \leq 1$), calcination of the precursor to obtain NiCo₂O₄, and converting of NiCo₂O₄ to NiCo₂S₄. The third step involves usually with gas-solid reaction by H₂S, S, Na₂S^[13-18] with the oxide to obtain the NiCo₂S₄.

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Electrochemical applications

Supercapacitor

As one type of the green energy, the outstanding merit of the SCs is the short charging time under high current density with high power density. Many parameters can influence such performance, and the electrode materials are one of the most key issues. NiCo₂O₄-based materials have been widely explored as the electrode materials for SCs for their excellent performance.^[19,20] When we change O of NiCo₂O₄ to S, the NiCo₂S₄ materials could be obtained with many characteristics: a flexible structure making easier for electrons transportation, high electric conductivity of 100 times than that of NiCo₂O₄. Such characteristics make NiCo₂S₄ possess remarkable specific capacitances. Up to now, nearly 2/3 of the published papers on NiCo₂S₄ are focused on the field of SCs. As pseudo-capacitance material, the following redox reactions happen during the charge-discharge process:

Very recently, Huang *et al.*^[11] published the first review paper on the application of NiCo₂S₄ in SCs, and they made a brief introduction on the structures and morphologies of the NiCo₂S₄ materials from 0D, 1D, 2D to 3D. In view of this, we will not discuss the development of the NiCo₂S₄ as electrode materials for SCs in details in this minireview. However, we must make one thing clear: NiCo₂S₄ is a kind of important electrode material possessing potential application in the area of SCs.

Li-ion batteries

In the past decades, intense research efforts have been made in the field of LIBs because of the outstanding merits (high energy and power densities) of LIBs as portable electronic devices.^[21] Owing to the lower cost and higher theoretical capacities, the transition metal disulfides are regarded as the promising electrode materials for LIBs.^[22,23] Recently, with the outstanding high conductivity of $1.25 \times 10^6 \text{ s} \cdot \text{m}^{-1}$, the bimetallic NiCo₂S₄ is emerging as the new candidate for the electrode material. When used anode material for LIBs, it is believed that the following reactions are involved:^[13]

Yu *et al.*^[24] claimed that they were the first to report NiCo₂S₄ as an anode for LIBs, and the material demonstrated high specific capacity (1296 mAh·g⁻¹) and extraordinary cycling stability (100% retention for 100 charge-discharge cycle). In fact, a little earlier than this paper, Hu *et al.*^[25] synthesized NiCo₂S₄ grown on carbon cloth as an anode for LIBs, and the hybrid material delivered high specific capacity (1275 mAh·g⁻¹) and excellent rate performance. At a current density of 1 A·g⁻¹, for 100 charge-discharge cycle, the retention is 89.2%. At about the same time, Jin *et al.*^[13] fabricated hierarchical NiCo₂S₄ hollow spheres, of which possessed a specific capacity of 696 mAh·g⁻¹ for 100 cycles (0.2 A·g⁻¹). Liu *et al.*^[26] prepared hierarchical nanostructured hybrids composed by NiCo₂S₄ nanosheets and nitrogen-doped graphene/carbon nanotube networks, and the composite material displayed high initial charge capacity of 1225.4 mAh·g⁻¹ (0.2 A·g⁻¹). Recently, Xu *et al.*^[27] reported NiCo₂S₄/Ni_{0.96}S nanoparticles anchored in 3D graphene aerogel, and the material has a superlong cycling stability of 620 mAh·g⁻¹ for 800 cycles (1 A·g⁻¹).

Hu *et al.*^[28] prepared NiCo₂S₄ hexagonal nanosheets, which delivered a high-rate and long-term cycle ability, and it had a high capacity of 607 mA·h·g⁻¹ after 800 cycles (2 A·g⁻¹). In conclusion, as the anode materials for LIBs, NiCo₂S₄ has high electrical conductivity, mechanical stability, and excellent cycle performance. However, such applications are still limited, and they are worth of further study (The comparison of recent published papers on LIBs is presented in Table 1).

Table 1 The LIBs performance of different NiCo₂S₄-based electrode

Sample	Current density/ (A·g ⁻¹)	Cycle number	Initial capacity/ (mAh·g ⁻¹)	Capacity retention /%	Ref.
NiCo ₂ S ₄ nanorod	0.1	100	1296	100	[24]
NiCo ₂ S ₄ nano-sheet/carbon cloth	1	100	1275	89.2	[25]
NiCo ₂ S ₄ hollow spheres	0.2	100	1251	55.6	[13]
NiCo ₂ S ₄ Nanosheet/graphene/carbon nanotube	0.2	100	1225.4	89	[26]
NiCo ₂ S ₄ /Ni _{0.96} S/graphene	0.1(1)	200(800)	966(677)	98.3 (91.6)	[27]
NiCo ₂ S ₄ nanosheet	2	800	747	81.2	[28]

Dye sensitized solar cells (DSSCs)

DSSCs have attracted increasing attention for the next-generation photovoltaic devices, possessing such merits as low-cost, easy preparation, transparency, and high power conversion efficiency.^[29,30] The counter electrode (CE) is one of the three key components of the DSSCs. The Pt-free CE materials are one of the hot research topics. Binary metal sulfides such as CoS, NiS, MoS, and so on, are considered as good candidate for CE materials. The working principle of DSSCs can be simply shown in Figure 2. For DSSCs, redox between I₃⁻ and I⁻ is very important. The NiCo₂S₄ material as the catalyst quickens the reaction rapidly.^[31,32]

Figure 2 The working principle of DSSCs.

The papers by Xiao *et al.*^[16] and Lin *et al.*^[12] might be the first two reports on the application of NiCo₂S₄ as CE for DSSCs. In Xiao's paper, they prepared a hollow NiCo₂S₄ single nanorod as CE and reported an efficiency of 4.2%. Lin *et al.*^[12] synthesized highly transparent NiCo₂S₄ thin film as CE and obtained an impressive efficiency of 6.14%, which is comparable to the efficiency of Pt (6.29%). Afterwards, several other studies are reported. Self-supported NiCo₂S₄ nanoneedles were deposited on fluorine-tin-oxide (FTO) glass as CE for DSSCs,^[15] showing an efficiency of 6.9% (vs. Pt with 7.7% efficiency). Interconnected NiCo₂S₄ nanosheets^[31] exhibited higher power conversion efficiency of 7.22% (vs.

Pt with 6.87% efficiency). Dendrite structured NiCo₂S₄ was fabricated by one-step electrodeposition method, and showed a higher efficiency than the conventional Pt CE.^[9] Wu *et al.*^[32] synthesized flower-like NiCo₂S₄/NiS microspheres by two-step hydrothermal method, and the CE materials shows a perfect PCE of 8.8% (vs. Pt with 8.1% efficiency). The Ni-Co-S particles with different compositions were prepared and used as CE for DSSCs,^[33] of which NiCo₂S₄ shows better performance. Murugan *et al.*^[34] developed NiCo₂S₄/graphene nanohybrid with a high power conversion efficiency of 7.98% (vs. Pt with 8.01% efficiency). Based on the above reports, NiCo₂S₄ shows better or comparable performance when used as CE for DSSCs, and thus it can be considered as promising Pt-free CE materials. The photovoltaic characteristics of DSSCs with NiCo₂S₄ as CE are shown in Table 2.

Table 2 Photovoltaic characteristics of DSSCs with NiCo₂S₄ as counter electrodes

Sample	$J_{sc}/(\text{mA}\cdot\text{cm}^{-2})$	V_{oc}/V	$FF/\%$	$\eta/\%$	Ref.
NiCo ₂ S ₄ nanorod	11.94	0.55	48.9	3.76	[16]
NiCo ₂ S ₄ film	14.11	0.72	60	6.1	[12]
NiCo ₂ S ₄ nanoneedle	13.38	0.76	63.2	6.9	[15]
NiCo ₂ S ₄ nanosheets	18.37	0.67	58.66	7.22	[31]
Dendrite structured NiCo ₂ S ₄	13.6	0.758	68.1	7.03	[9]
NiCo ₂ S ₄ /NiS microspheres	17.7	0.744	67	8.8	[32]
NiCo ₂ S ₄ particle	17.17	0.69	63	7.43	[33]
NiCo ₂ S ₄ /graphene	15.62	0.72	70.5	7.98	[34]

Hydrogen evolution reaction (HER)

Hydrogen is a clean resource without any pollution, and electrochemical water splitting is the most efficient method to produce hydrogen, during which process requires catalyst for cathodic HER. Pt related materials are the most effective catalyst. To replace the noble metal Pt, many other low-cost catalyst have been widely researched, and transition metal dichalcogenides behaved promising activity and stability.^[23] Similarly, NiCo₂S₄ is reported to be a kind of effective catalyst for HER (Table 3). Recently, Lu *et al.*^[35] prepared NiCo₂S₄ nanowires on carbon cloth by topotactic conversion of NiCo₂O₄ and tested the HER activity. The result showed that the nanowire produced 100 mA·cm⁻² at an overpotential of 305 mV. Li *et al.*^[36] constructed NiCo₂S₄ nanowires over 3D graphdiyne foam, and the catalyst exhibits an onset overpotential of only 112 mV with excellent durability for 80 h without negligible loss. Using Ni foam as the current carrier, Jin *et al.*^[37] synthesized NiCo₂S₄ nanoflakes by sulfidation of NiCo-LDH, and the materials exhibited an onset overpotential of 17 mV, the overpotential at current density of 10 mA·cm⁻² is 65 mV. Shanmugam *et al.*^[38] loaded directly NiCo₂S₄ nanowires on Ni foam, and the catalyst delivered a current density of 10 mA·cm⁻² at overpotentials of 210 m. Using the same current carrier, the NiCo₂S₄@NiFe LDH was applied as the HER catalyst, and the low overpotential of 200 mV was required at the current density of 10 mA·cm⁻². When used as the catalyst for HER, the electrolyte can be alkaline (KOH) or acidic (H₂SO₄) solution, and the corresponding mechanism is different. For the HER in alkaline media, the following reaction are involved.^[37,39]

The electroreduction of water and hydrogen adsorption

The electrochemical hydrogen desorption

and/or the chemical desorption

where M is the metal atom, and H_{ads} stands for H absorbed at the active site of catalyst. However, the HER mechanism in acidic solution involves:^[7]

Based on the above result, we think that the NiCo₂S₄ based materials are one of the most suitable catalysts for HER with exceptional stability. However, the research is limited, and it needs further research.

Table 3 Comparison of the HER performances of the NiCo₂S₄ electrocatalyst

Sample	Over potential @-10 mA·cm ⁻² /mV	Tafel slope/ (mV·dec ⁻¹)	Stability	Ref.
NiCo ₂ S ₄ nano-wires/carbon cloth	230	141	Almost stable for 12 h	[35]
NiCo ₂ S ₄ /graphdiyne	112	99	80 h	[36]
NiCo ₂ S ₄ nanoflakes/Ni foam	65	84.5	Slightly increased after 100,000 s	[37]
NiCo ₂ S ₄ nanowires/Ni foam	210	58.9	50 h, 10% decrease	[38]
NiCo ₂ S ₄ @NiFe LDH	200	101.1	12 h	[40]

Oxygen reduction reaction (ORR) and oxygen evolution reaction (OER)

ORR and OER are two important oxygen-related reactions that are involved in the metal-air batteries and fuel cells.^[41] During such process, efficient catalysts are needed to have a high electrocatalytic activity. Transition metal chalcogenides are regarded as one of the effective and low cost catalysts. Among them, bimetallic NiCo₂S₄ have been reported to perform excellent ORR and OER activities. For instance, the hybrid of NiCo₂S₄@graphene was used firstly as a bifunctional electrocatalyst for ORR and OER.^[3] The catalyst displayed less reduction activity but superior methanol tolerance for ORR. Impressively, it showed higher OER activity. The NiCo₂S₄ sub-micron spheres^[42] and hydrangea-like NiCo₂S₄^[43] were also reported to be an efficient electrocatalyst for ORR and OER. Although there are a few studies claims that the NiCo₂S₄ is good catalyst for ORR,^[44-46] the ORR activity is actually not so outstanding compared with other kind of catalysts. It is more suitable to be used as the catalyst for OER. For example, the porous NiCo₂S₄ showed a low overpotential of 337 mV (10 mA·cm⁻²) with a low Tafel slope of 64 mV, and it exhibited long-term stability for two thousand cycles.^[47] Nevertheless, there raised an argument that the metal chalcogenides should not be considered as the OER catalyst.^[48] This is because that the metal chalcogenides are not stable under oxidizing potentials. They could be converted to metal oxides/hydroxides which itself are good catalysts for OER. The in-situ formed metal oxides/hydroxides are the true active center of the OER as the following equations showing.^[38]

Thus, Jin^[48] suggested that the metal chalcogenides should be named as the pre-catalyst for OER.

Strategies to improve the performance

The electrochemical performance of the NiCo₂S₄ materials can be affected by many parameters: morphology, size, structure/architecture, composition, *etc.* Thus we can tune its activity by controlling the morphology, structure, composition and current carrier.

Morphology

The shape/structure has great effect on the electrochemical performance because different shape might endow the material with various surface area, pore size distribution, defects, and charge resistance. The above properties can influence the electrolyte/electrode contact area, the electrolyte flowing and ion transportation, the reaction active sites, and finally affect the performance. Therefore, a great deal of NiCo₂S₄ with various morphology have been prepared.^[1] Among numerous shape, the hollow structured NiCo₂S₄ is worth of enough attention because of such features as distinguishable interior voids, large surface area, and the reduced transport route. In this area, Lou group did brilliant work.^[49] However, the systemic research of the morphology effect of NiCo₂S₄ in the same or similar reaction system is still rare except that reported by Hu^[50] and Zhang *et al.*^[51]

Structure

The combination of NiCo₂S₄ with other materials to construct hierarchical architectures can produce rich pore (micro or meso) and induce the so-called synergistic effect among different components,^[52] which can finally affect the electrochemical performance. Up to now, various NiCo₂S₄-based nanocomposites have been fabricated, such as NiCo₂S₄@Ni(OH)₂,^[53,54] carbon@NiCo₂S₄,^[55] NiCo₂S₄@CoS_x,^[56] NiCo₂S₄@Co₉S₈,^[6] CoS@NiCo₂S₄,^[57] NiCo₂S₄@PPy,^[58] MWCNT-COOH@NiCo₂S₄,^[59] NiCo₂S₄@Ni₃S₂,^[60] NiCo₂S₄/Ni_{0.96}S,^[27] Ni_x-Co_{3-x}S₄/Ni₃S₂,^[61] NiCo₂S₄@MnO₂,^[62-64] NiCo₂S₄@NiMoO₄,^[65] NiCo₂S₄@NiO,^[66] NiCo₂S₄@NiFe LDH,^[67] NiCo₂O₄/NiCo₂S₄,^[68] Ni_xCo_{3-x}S₄@NiCo₂O₄,^[69] *etc.*

Composition

NiCo₂S₄ has a spinel structure with AB₂S₄ formula, and its composition can be tuned in certain range. For one aspect, we can change the molar ratio of Ni to Co, for example, CoNi₂S₄,^[50,70-72] Ni_{3-x}Co_xS₄.^[73-75] For another aspect, the element in A and B position can be changed to other transition metals, such as MnCo₂S₄,^[76,77] CuCo₂S₄,^[78,79] FeNi₂S₄.^[80] Through such modification, the electrochemical performance of the NiCo₂S₄ related materials can be tuned.

Current carrier

The direct incorporation of NiCo₂S₄ with conductive networks can avoid the use of insulating binder, decrease the contact resistance, favor for the mass/charge transport, thus it will facilitate the electrochemical performance. The current carrier including carbon materials (porous carbon, carbon fiber cloth, carbon fiber paper, graphene),^[35,69,81,82] Ni foam.^[37,38,83] The carbon materials offer many advantages: low-cost, flexible, lightweight, richness in pore. The carbon materials can be modified by non-metal element B, N, S, P to further increase the activity as both the substrate and active sites. For

porous carbon, the pore size can be controlled by preparation parameters. All those characteristics make the carbon material be good candidates as the current carrier for NiCo₂S₄. The Ni foam has better mechanical strength, higher conductivity, relatively superior corrosion stability in alkaline solution. One thing to note is that the surface of Ni foam could be partly passivated when exposed to air for time, and necessary pretreatment should be taken to activate and clean the surface.^[84]

Summary and prospective

In summary, the studies about NiCo₂S₄ have witnessed soaring growth especially in the past three years, and the achievements are remarkable in view the wide application of NiCo₂S₄ in several electrochemistry related fields. However, there is still a great space for the development of the NiCo₂S₄-based materials. The preparation method is limited, and innovative manufacturing processes achieving large-scale production should be developed to meet the demand of the industrial applications. Furthermore, the studies are not in-depth, the majority of the papers are experimental observations and explanation, the fundamental understanding of the relationship between structure/performance is still lacking. The theoretical simulation and *in-situ* observation should be further applied. Finally, it is expected that the NiCo₂S₄ materials might have potential application in other research area (as a catalyst for heterogeneous reaction).

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