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Chapter

Supercapacitor Supported by Nickel, Cobalt and Conducting Polymer Based Materials: Design Techniques and Current Advancement

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Abstract

The recent advanced electronic appliances demand special high power devices with lightweight, flexible, inexpensive, and environment friendly in nature. In addition, for many industrial and automotive applications, we need energy storage systems that can store energy in a short time and deliver an intense pulse of energy for long duration. Till date the Li-ion battery is the only choice for fulfilling all our energy storage demands. However, the high cost, limited availability and non-environmental nature of electrodes and electrolyte material of Li-ion battery limits its applicability. Hence, the world demands an alternative replacement for the Li-ion battery. In this regard, the supercapacitor is one of the most emerging and potential energy storage devices. The electrode plays an important role in supercapacitors. The nickel and cobalt based oxide, hydroxides, and their composites with conducting polymer are promising and highly appreciated electrode materials for supercapacitors. This chapter covers the recent advances in supercapacitors supported by nickel, cobalt and conducting polymer based materials and their applications predominantly described in the recent literature. Recent advances are reviewed including new methods of synthesis, nanostructuring, and self-assembly using surfactant and modifiers. This chapter also covered the applications of supercapacitors in powering the light weight, flexible and wearable electronics.

Keywords: supercapacitors, mixed ternary metal oxides, nanostructured, NiCo_2O_4 , energy density, etc.

1. Introduction

Supercapacitor (SCp) is also known as ultracapacitor. SCP is the advanced electrochemical energy storage device. At present, the lithium ion battery (LiBs), lead acid battery and SCP are the major available energy storage systems. Over the other energy storage systems, the SCP is stands out to be a promising energy storage device with very attractive properties such as high specific capacitance, high power density, moderate energy density, good cyclic stability, low cost, environmental friendly nature, etc. SCP has been utilized in various electrical applications viz.

hybrid vehicles, power backup, military services, and portable electronic devices like laptops, mobile phones, roll-up displays, electronic papers, etc. [1–3].

The performance of SCP is strongly depends on types electrode materials i.e. active material used in supercapacitor. Based on the type of active material used and process energy storage, the SCP can be divided into three main categories, including pseudocapacitors (PCs), electric double-layer capacitors (EDLCs) and hybrid capacitors [4–6]. In PCs metal oxides, metal hydroxides and conducting polymers are employed as active material. On the other hand, carbon base materials such carbon nanotubes, graphene and carbon black, etc. are used as active material in EDLCs employed. Likewise, the used of combination of metal oxide, conducting polymer and carbon based material as active material results hybrid capacitor. The PCs delivered high specific capacitance, high energy density than EDLCs, but demonstrates poor power density and cycle stability. Nevertheless, owing to the high active surface area, the EDLCs delivered high specific capacitance but suffer poor energy density than PCs [4]. The hybrid capacitors retain the advantage of both PCs and EDLCs and hence they delivered high specific capacitance, high energy density, and large cycle life [7, 8]. Moreover, the performance of supercapacitors is equally rely on different aspect of active material viz. quality, electric conductivity, material, size, porosity, synthesis method, etc. More specifically, the synthesis method can bring many attractive advantages in active material for extraordinary electrochemical performance of supercapacitor. Therefore, synthesis of active materials with high porosity, stable performance and good electrical conductivity has a very wide research potential.

Recently, to enhance the energy density, cycle life and electrochemical performance of the supercapacitors, the use of electrode material with desired structure with uniform porosity is one of the appealing strategies. From many decades, the nanostructured single transition metal oxides such as RuO_2 [9], MnO_2 [10], CeO_2 [11], Fe_2O_3 [12], Fe_3O_4 [13], Co_3O_4 , Mn_3O_4 , etc., and the nanostructured mixed ternary metal oxide (TMOs) such as ZnFe_2O_4 , NiFe_2O_4 , CuFe_2O_4 , CoFe_2O_4 , MnCo_2O_4 , ZnCo_2O_4 , NiCo_2O_4 , and etc., and conducting polymers such as, polyaniline (PANi), polypyrrole (Ppy), polythiophene (Pth), etc. has been extensively used as active material for all types of supercapacitors. Out of the different materials used as the electrodes for SCP applications. The TMOs are highly studied and excessively used as active material in all types of supercapacitors. The mixed TMOs are also called the spinel metal oxide. The spinel TMOs have the general formula AB_2O_4 . In AB_2O_4 , the cubic crystal structure of TMOs consists of closely packed O^{2-} anions and an octahedral and tetrahedral space of the lattice occupied by the transition metal cations A and B, respectively. Due to this closed packed structure, the mixed TMOs show the extraordinary characteristics over single metal oxides, such as two order higher electrical conductivity, superior electrochemical performance and excellent stability over single metal oxides. Moreover, the recent research reports shows the TMOs have better structural advantages and higher surface area and porosity [14]. More specifically, the TMOs show low cost, natural abundance, low toxicity and environmental friendly nature. Hence, TMOs have drowned more research attention in recent years. In addition, the extraordinary electrochemical performance of TMOs in solid as well liquid electrolyte makes it a promising and potential candidate as electrode material for PCs. The various mixed TMOs viz. ZnFe_2O_4 , NiFe_2O_4 , CuFe_2O_4 , CoFe_2O_4 , MnCo_2O_4 , ZnCo_2O_4 , NiCo_2O_4 , etc. has been utilized as electrode material for PCs. Out of the different TMOs the nickel and cobalt based TMOs have gained more research attention as electrode material in supercapacitors due to their attracting properties such as low cost, natural abundance, low toxicity and environmental friendly nature. More specifically, these materials show variable structures, diverse morphologies, high specific surface and uniform porosity and outstanding

electrical conductivity. The NiCo_2O_4 demonstrated high electrical conductivity due to the presence of Ni in it. Whereas, Co enhances the electrochemical activity of oxides, further, the synergistic effect among Ni in Co offers high electrical conductivity with an excellent electrochemical behavior in supercapacitors [12]. The NiCo_2O_4 demonstrated a high theoretical capacity [15]. The nickel and cobalt based TMOs show diverse morphologies, this includes various nanostructures ranging from 0 to 3 D architectures viz. quantum dots, nanowires, nanosheets, platelets like nanoparticles, porous network like framework, coral-like porous crystals, ordered mesoporous particles, urchin-like microstructures and urchin-like nanostructures. Till date many recent attractive reviews have presented recent development in mixed TMOs as electrode material for SCs [7, 16–19]. We recommend few of them for readers who are new to this field of energy research.

In the present chapter we provide the recent advancements in synthesis of nanostructured nickel and cobalt base mixed TMOs and their composites with conducting polymer based materials as electrode material for supercapacitors predominantly described in the recent literature. Moreover, here our special emphasis will be on new methods of synthesis, nanostructuring, and self-assembly using surfactant and modifiers. In addition, we provide a summary of structural and morphological advancements regarding the electrochemical properties of supercapacitors. Finally, we link our discussion to the recent applications in powering the light weight, flexible and wearable electronics real world applications.

2. Synthesis of nickel and cobalt base mixed TMOs

Compared to the micro sized the nanostructured cobalt and nickel based TMOs show higher specific capacitance and long cycle life. Therefore many recent research strategies have drowned to synthesized nanosize mixed cobalt and nickel based TMOs. The various synthesis methods for synthesis of nanostructured cobalt and nickel based mixed TMOs viz., hydrothermal method sol-gel, thermal evaporation method, chemical bath deposition, electrodeposition, oil/water interfacial self-assembly strategy, etc. have been extensively reported in literature. Hydrothermal method is one of the excessively adopted synthesis methods for hierarchical nanostructure synthesis. This method is cost effective, simple, and easy to scale-up at room temperature. This method is mostly used for fine tuning the morphology and controlling the size of nanostructures. Agglomeration of NiCo_2O_4 results in low electrical conductivity and decreases the specific capacitance and cycle life of SCp [20]. Therefore, to enhance the electrical conductivity the use of high surface area with high porosity conductive substrates are highly recommended. These substrates enhance the contact between electrode and electrolyte and allowed more electrolyte ions penetration in active material. The various conductive substrates such as textiles, sponges, carbon clothes, carbon fibers, conventional paper, cables, etc. are used as substrates to fabricate SCs. Such conductive substrates are advantageous for enhancing the electrochemical performance via providing short diffusion path, high electrical conductivity, ample electroactive sites [21]. In this regard, Yang *et al.* synthesized the nanoneedle arrays of on filter carbon paper substrate via facial hydrothermal synthesis method. For fabrication the filter carbon paper submerged into the precursor of NiCo_2O_4 followed by calcination in the Argon atmosphere in the range of 250–400°C for 2 hours. Using this approach they have reported urchin like and nanoneedle arrays and further adopted this nanostructure for SCp applications [20]. The synthesis parameters like reaction temperature reaction temperature and reaction time controls the structures. Further, the calcination temperature after synthesis plays crucial role in improving the surface morphology, specific surface

area, porosity, etc. [22]. Siwatch *et al.* [22] have reported the formation of NiCo₂O₄ quantum dots via hydrothermal synthesis and studied the effect of synthesis parameters like reaction temperature and time, and calcination temperature on the morphology of NiCo₂O₄ quantum dots. Further, the highly porous flower-like structure of NiCo₂O₄ quantum dots obtained at the calcination temperature 300° C is highly useful for SCp applications. Lu *et al.* reported the synthesis of mesoporous NiCo₂O₄ via reagents assisted hydrothermal method and studied the effect of reagent cetyltrimethylammonium bromide (CTAB) on morphology and electrochemical behavior of NiCo₂O₄ for SCp applications. Moreover, the reagent during synthesis enhanced the specific surface area and charge transport of NiCo₂O₄. As a result, the cyclic stability, rate performance and specific capacitance of NiCo₂O₄ quantum dots based in asymmetric SCp found to be increased [23]. Binder used during the fabrication of electrode increase the electrode resistance which further decreases the electrochemical performance and cycle life of SCp. Therefore recently binder free fabrication approaches such as direct growth on conductive substrate is more popular. Furthermore, over the conventional substrates the direct growth on three dimensional (3D) conductive substrate offers many advantages such as shorten the diffusion path, healthy synergy between the active material and electrolyte, provides ample electroactive site, etc. which further help to enhance the electrochemical performance of SCp. For example, Yang *et al.* [24] directly grown NiCo₂O₄ on gelatin-based carbon nickel foam (3D) by facial hydrothermal method followed by calcination at 350°C for 2 hrs under an Argon atmosphere.

The morphology of NiCo₂O₄ is reported to be nanoflower-like. The fabricated 3D electrode provides fast ions and electrons transfer rate and enhances the electroactive surface area of the NiCo₂O₄ via forming a complex 3D network. In addition, the nickel foam as substrate adds the electric conductivity whereas the gelatin based carbon on the nickel foam provides high surface area for uniform growth of NiCo₂O₄ during synthesis. In our previous study, we have reported the synthesis of nanostructured NiCo₂O₄ via surfactant assisted hydrothermal method and studied the effect surfactant and reaction parameters on the morphology of nanostructured NiCo₂O₄. From this synthesis, we got two distinct morphologies viz. platelet-like and nanorod-like using surfactants TEA ethoxylate and polyethylene glycol (PEG), respectively. We further used this nanostructured NiCo₂O₄ for SCp applications [18].

In addition to the hydrothermal method, the combustion method is one of the simple and easy to scalable synthesis methods. Over the hydrothermal method the combustion method does not requires Teflon-lined stainless steel autoclaves and centrifuge for product washing, is less time consuming and provides high phase purities. This regard, Kumar *et al.* reported the growth of NiCo₂O₄ on conductive substrate nickel foam using combustion method. For the synthesis, honeycomb-like NiCo₂O₄ the nitrate and glycine used as oxidizer and fuel, respectively. [6]

For enhancing the surface area and porosity and electrochemical activities of NiCo₂O₄, the formation of composites of NiCo₂O₄ with carbon based material is one of the appealing strategies, for example, NiCo₂O₄/CNT, NiCo₂O₄/MWCNT, NiCo₂O₄/graphene, NiCo₂O₄/reduced graphene oxides (r-GO), etc. demonstrated to be a potential candidates for SCp applications. Carbon base material viz. CNT, MWCNT, graphene, r-GO, etc. provide excellent flexibility, high specific surface areas, remarkable electrical conductivity, good thermal and chemical stability [5, 25–27]. For example, Li *et al.* [25]. reported the synthesis of NiCo₂O₄/CNT composites, and studied the structure formation of NiCo₂O₄ with and without surfactant for supercapacitive applications. The nanoflakes and nanocorn like morphology for NiCo₂O₄ is obtained by using surfactant sodium dodecyl sulfate. Pathak *et al.* synthesized NiCo₂O₄ and NiCo₂O₄@ MWCNT composite using facile hydrothermal method.

NiCo₂O₄@ MWCNT demonstrated superior electrochemical performance and demonstrated a good electrode for SCp applications. In addition, using density functional they reveal the enhanced density of states near the Fermi level and increased quantum capacitance of the NiCo₂O₄ @SWCNT is one of the important reasons for high specific capacitance, high power density and energy density [28]. The PCs use reversible fast faradaic reactions to store electrical charges, which allow them to achieve higher capacitance by at least one order of magnitude than those obtained by EDLCs. Materials sustaining such redox reactions on their surfaces include, for example, conducting polymers and transition metal oxides.

3. Applications of Ni and Co based metal oxides and their composites

3.1 Pseudocapacitor (PCs)

Recently, PCs received considerable attention due to the one order higher capacitance, higher volumetric capacitance, higher energy density and use of low cost and easily synthesized active material than EDLCs. [28–30]. For example, Eskandari *et al.* fabricated NiCo₂O₄ and its composite with PANi and MWCNTs and reduced graphene oxide r-GO and studied their SCp performance in 3 M KOH. Out of the different composites the NiCo₂O₄/PANi demonstrated superior performance and exhibited specific capacitance of 1760 Fg⁻¹ (900 F/g and 734 F/g for NiCo₂O₄/ MWCNTs and NiCo₂O₄/r-GO, respectively) at current density of 1 Ag⁻¹, respectively. The highest specific capacitance in NiCo₂O₄/PANi is due to supplementary conductive pathways provided by PANi and synergistic effect of the rooted pseudo-reaction. Moreover the composite NiCo₂O₄/MWCNTs shows stable cycle is life and demonstrated to be best retention over all other composites as 89% over 2000 charge discharge cycles. Composite NiCo₂O₄ /r-GO also exhibited good cycle performance and shows retention in specific capacitance of 87% over 2000 charge discharge cycles. In addition, the pristine NiCo₂O₄ shows higher retention than NiCo₂O₄/PANi, i.e. 70% and 73%, respectively. The highest cyclic stability in NiCo₂O₄/MWCNTs is due to the high electrical conductivity and high mechanical strength of MWCNTs. In fact, the good cyclic performance in NiCo₂O₄/r-GO is the results of higher electrical conductivity, high surface morphology and good mechanical strength than PANi and pristine NiCo₂O₄ [31] Moreover, the representative Ni and Co based material and their performance in PCs are summarized in **Table 1**.

3.2 Hybrid capacitors

Even if the Ni and Co based TMOs are advantageous for SCp applications, however, in the long cycling process the rapid degradation of NiCo₂O₄ electrode materials is the major obstacle among the commercialization of NiCo₂O₄ based SCp. By increasing the electrical conductivity of NiCo₂O₄ this hurdle can be minimized and the higher rate capabilities can be attained. Therefore, from the last two decades, researchers devoted more efforts to enhance the electrical conductivity of NiCo₂O₄, this includes fabrication of hybrid composite with other conducting electrode materials, viz. carbon based material (CNTs, SWCNTs, MWCNTs, activated carbon, doped and undoped reduced graphene oxides, etc.), conducting polymers, etc. In addition, recent formation of composite of NiCo₂O₄ with other mixed TMOs has gain enormous attention. For example, Mary *et al.* reported the fabrication of NiCo₂O₄ and ZnCo₂O₄ composites and studied their morphology dependent electrochemical behavior for hybrid SCp applications. In addition, the hybrid SCp

Sr. No.	Material	Method of synthesis	Electrolyte	Voltage window (V)	Specific capacitance (Fg ⁻¹) at current density-scan rate	Energy density Whkg ⁻¹	Retention of capacitance at (current density) (cycle numbers)	Reference
1.	NiCo ₂ O ₄	Hydrothermal	1 M Na ₂ SO ₄	0–0.6 V	479/ 5 mVs ⁻¹	21.3	87.21% (5000)	[30]
2.	NiCo ₂ O ₄	Hydrothermal	1 M Na ₂ SO ₄	0–0.4 V	320 0.1 mVs ⁻¹	16.1	95.34%, (1000)	[32]
3.	NiCo ₂ O ₄ /NiCo ₂ S ₄	Molecular design	—	0.1–0.6 V	1296 1 Ag ⁻¹	44.8	93.2% (6000) 10 Ag ⁻¹ ,	[1]
4.	NiCo ₂ O ₄	Hydrothermal	3 M KOH	0.0–0.6 V	3143 2 mVs ⁻¹	56	48% (5000) 10 Ag ⁻¹ ,	[33]
5.	NiCo ₂ O ₄ @α-Co(OH) ₂ nanowires	Hydrothermal	2 M KOH	–0.2 -0.5 V	1298-1 Ag ⁻¹	39.7	83% (5000) 2 Ag ⁻¹	[34]
6.	Mesoporous NiCo ₂ O ₄ nano-needles	Hydrothermal	—	0.0–0.5 V	1410 Fg ⁻¹ -1 Ag ⁻¹		94.7% (3000) 20 Ag ⁻¹	[35]
7.	NiCo ₂ O ₄ nanosheets	Solvothermal	—	—	2690 Fg ⁻¹	52.6	80.9% (3,000) 20 mA cm ⁻² .	[36]
8.	NiCo ₂ O ₄ PANi	Hydrothermal and in-situ polymerization	6 M KOH	0–0.5 V	3108 1 mA·cm ⁻² .	77.57	96.1% (1000)	[37]
9.	NiCo ₂ O ₄ nanoneedles	Hydrothermal via annealing approach	1 M KOH	0–0.7 V	1076 0.5 Ag ⁻¹	30.5	14% (1000) 10 Ag ⁻¹	[38]
10.	NiCo ₂ O ₄ nanoneedles	Pulsed laser ablation	3 M KOH	0–0.6 V	1650 Fg ⁻¹ 1 Ag ⁻¹	56.7	91.78%, (12,000) 10 Ag ⁻¹	[39]

Table 1.
Overview of representative Ni and Co based material and their performance in PCs.

Sr.No.	Material	Method of synthesis	Electrolyte	Voltage window (V)	Specific capacitance (Fg^{-1}) at current density/ scan rate	Energy density Whkg^{-1}	Retention of capacitance (cycle numbers) at current density	Reference
1	NiCo_2O_4 CNT	Hydrothermal	2 M KOH	-0.1- 0.5	574.3 0.5 Ag^{-1}	—	111.5% (1000)	[25]
2	NiCo_2O_4 @MWCNT	Hydrothermal	0.5 M K_2SO_4	—	374 2 Ag^{-1}	95	74.85% (3000)	[28]
3	3D NiCo_2O_4 /MWCNT	Sol-gel	2 M KOH	0-0.5 V	1010 0.1 Ag^{-1}	37.7	83.4% (2000) 2 Ag^{-1}	[40]
4	Ordered Mesoporous Carbon/ NiCo_2O_4	co-precipitation	6 mol· L^{-1} KOH	0-0.6 V	577.0 1 Ag^{-1}	—	92.7%. (2000) 2 Ag^{-1} ,	[41]
5	NiCo_2O_4 - nanoporous carbon.	Chemical	1 M KOH	-0.2-0.6 V	89 $0.1 - \text{Ag}^{-1}$	28	85% (2000)	[42]
6	Mesoporous carbon - NiCo_2O_4	hydrothermal followed by calcination	3 M KOH	-0.45-0.45	204.28 $1 - \text{Ag}^{-1}$	5.75	90.35% (3000) 20 Ag^{-1}	[43]
7	Hallow bamboo-shaped NiCo_2O_4	Template	6 M KOH	0.0-0.6 V	680.1 C g^{-1} 1 Ag^{-1}	59.82	99.7% (5000) 10 Ag^{-1} .	[44]
8.	rGO- NiCo_2O_4 quantum dots	Chemical	1 M Na_2SO_4	0.0-1.6 V	265 0.73 Ag^{-1}	47	69% (1000)	[45]
9.	Oxygen-vacancy-rich NiCo_2O_4 /nitrogen-deficient graphitic carbon nitride hybrids	Chemical	6 M KOH	0.0-0.6 V	1998 2 Ag^{-1}	70.22	95.22% (5000)	[46]
10	NiCo_2O_4 @Ppy/CC	Hydrothermal	2 M KOH	0.0-0.5 V	155.4 mAh g^{-1} 1 mA cm^{-2}	22.3	71% (8000) 10 mA cm^{-2}	[47]

Table 2. Overview of representative Ni and Co based material and their performance hybrid supercapacitor.

Sr. No.	Material	Method of synthesis	Electrolyte	Voltage window (V)	Specific capacitance (Fg^{-1}) at current density/ scan rate	Energy density Whkg^{-1}	Retention of capacitance (cycle numbers) at current density	Reference
1	NiCo ₂ O ₄ /C composites // activated carbon (AC)	Hydrothermal	6 M KOH	0–1.4 V	995.2 10 Ag^{-1} ,	20.87	83.04% (5000) 100 mVs^{-1}	[20]
2	NiCo ₂ O ₄ quantum dots // reduced graphene oxide (rGO)	Hydrothermal	1 M Na ₂ SO ₄	0–2.4 V	362, 0.5 Ag^{-1} .	69.5	86% (1000)	[22]
3	NiCo ₂ O ₄ //AC	Hydrothermal	—	0–0.5 V	153.2 (1 Ag^{-1}),	22.5	97.1% (1000) 1 Ag^{-1}	[23]
4	NiCo ₂ O ₄ / gelatin-based carbonenickel foam // AC	Hydrothermal	—	0–0.5 V	1416 (1 Ag^{-1})	48.6	88.5% (10,000) 5 Ag^{-1} .	[24]
5	NiCo ₂ O ₄ @Ni foam// sugar-derived carbon (SC)	Combustion	6 M KOH	0–0.5 V	169, 1.5 Ag^{-1}	48	96.5% (3000)	[6]
6.	MWCNTs intermingled NiCo ₂ O ₄ // Cu ₂ WS ₄	Hydrothermal	3 M KOH	0–0.5 V	116 mAh g^{-1} , 1 Ag^{-1}	87	~88%, (10,000)	[5]
7.	NiCo ₂ O ₄ nanoparticles and nanowires	Hydrothermal and wet chemical	1 M Na ₂ SO ₄	0–1.6 V	1066.03 Ag^{-1}	59.56	77% (5000) 6.66 Ag^{-1}	[48]
8	NiCo ₂ O ₄ - carbon nanofiber	—	2 M KOH	—	991.96 5 Ag^{-1}	37.23	97.02% (3000) 30 Ag^{-1}	[15]
9	NiCo ₂ O ₄ / r-GO	Hydrothermal	1 M KOH	0.0–1.6 V	702 0.5 Ag^{-1}	—	92% (1000) 4 mA cm^{-1}	[49]
10	NiCo ₂ O ₄ / rGO	Co-precipitation	1 M KOH	0.0–0.6 V	1380 1 Ag^{-1}	—	90% (1000) 5 Ag^{-1} after	[50]

Table 3.
Overview of representative Ni and Co based material and their performance asymmetric supercapacitor.

fabricated using the NiCo_2O_4 and ZnCo_2O_4 composite and nitrogen doped activated carbon. The high surface area and uniform porosity of activated carbon in hybrid SCp enhances the capacitance via enabling the more electrolyte ions into active material. Interestingly, $\text{NiCo}_2\text{O}_4 @ \text{ZnCo}_2\text{O}_4$ composite shows high specific capacitance of 236 C g^{-1} at a current density of 1 A g^{-1} . Moreover, the aforementioned hybrid SCp results in high energy density of 101.6 Whkg^{-1} and high retention in capacitance at 78.5% over 12000 charge–discharge cycles. Moreover, the representative Ni and Co based material and their performance in hybrid SCp are summarized in **Table 2**.

3.3 Asymmetric capacitors

The symmetrical SCp limits their specific capacitance due to narrow potential windows. Moreover, the use of aqueous base liquid electrolyte in symmetrical SCp decreases the specific capacitance energy density and cycle life. To overcome such drawback the fabrication of SCp with two different kinds of active material based electrode is demonstrated to be an effective strategy. The SCp fabricated using two different electrodes is termed an asymmetric supercapacitor. In asymmetric SCp positive electrode is fabricated using metal oxide base material, while negative electrode is fabricated by carbon based material. The combination of different active materials in a single device with higher operating potential result in higher the specific capacitance and energy density [40]. However, aqueous-based symmetric supercapacitors suffer from narrow potential windows, due to the limitation of the water decomposition. Therefore, an effective way is to construct asymmetric supercapacitor, which consists of two kinds of electrode materials, for instance positive electrode having pseudocapacitive nature and negative electrode having electric double layer capacitance with higher operating potential, for obtaining higher energy density [19, 20]. In the case of positive electrode materials, transition metal oxide based nanoparticles, conducting polymers based materials have been widely utilized, which exhibits pseudocapacitance as well as reversible redox Faradaic reaction. As negative electrode materials, carbon based materials like carbon nanotubes (CNT), graphene oxide (GO), activated carbon, and mesoporous carbon materials displaying electric double layer capacitance have been used. Among the carbon allotropes, mesoporous carbons have been extensively used as negative electrode material due to its high surface area and good electrical conductivity. For more understanding the recent advancements in NiCo_2O_4 and their composites and their performance in asymmetric SCp are summarized in **Table 3**.

4. Conclusions and outlooks

With ever increasing energy demands, day by day the SCp gaining much interest as an energy storage device. From a many years, the nickel and cobalt based TMOs and their composites have been studied and successively employed as an active material in all types of SCp. The nanostructured NiCo_2O_4 is low cost, in abundance, environmentally friendly in nature and has high electrical conductivity. In addition, due to the enhanced mobility of charge carriers the nanostructured NiCo_2O_4 demonstrated to be higher electrochemical performance than the single metal oxides. In this regard, the recent advances in synthesis of pristine NiCo_2O_4 and their composites with diverse morphologies and their applications for electrochemical performance in all types of SCp have been summarized in this chapter. Out of the different synthesized methods used for synthesis nanostructured NiCo_2O_4 , the hydrothermal method is found to be excessively used. Moreover, the hydrothermal

method is demonstrated to be more advantageous for the synthesis of diverse morphologies ranging from 0 D to 3 D, and resulted in high specific surface area and uniform porosity. The pristine nanostructured NiCo_2O_4 has many limitations for its commercial supercapacitor applications. Therefore, advanced strategies like synthesis of hierarchical nanostructures of NiCo_2O_4 and the fabrication of composite with other mixed TMOs, carbon based material and conducting polymers can enhance the specific capacitance, energy density and rate capability of Ni and Co based supercapacitors.

Conflict of interest

The authors declare no conflict of interest.

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References

- [1] Y. Liu, Z. Wang, Y. Zhong, M. Tade, W. Zhou, Z. Shao, Molecular Design of Mesoporous NiCo₂O₄ and NiCo₂S₄ with Sub-Micrometer-Polyhedron Architectures for Efficient Pseudocapacitive Energy Storage, *Advanced Functional Materials*. 27 (2017) 1701229. doi:10.1002/adfm.201701229.
- [2] S.J. Uke, V.P. Akhare, D.R. Bambole, A.B. Bodade, G.N. Chaudhari, Recent advancements in the cobalt oxides, manganese oxides, and their composite as an electrode material for supercapacitor: A review, *Frontiers in Materials*. 4 (2017) 21.
- [3] S.J. Uke, G.N. Chaudhari, Y. Kumar, S.P. Mardikar, Tri-Ethanolamine-Ethoxylate assisted hydrothermal synthesis of nanostructured MnCo₂O₄ with superior electrochemical performance for high energy density supercapacitor application, *Materials Today: Proceedings*. (2020).
- [4] J.-S.M. Lee, M.E. Briggs, C.-C. Hu, A.I. Cooper, Controlling electric double-layer capacitance and pseudocapacitance in heteroatom-doped carbons derived from hypercrosslinked microporous polymers, *Nano Energy*. 46 (2018) 277-289.
- [5] V. Sharma, S.J. Kim, N.H. Kim, J.H. Lee, All-solid-state asymmetric supercapacitor with MWCNT-based hollow NiCo₂O₄ positive electrode and porous Cu₂WS₄ negative electrode, *Chemical Engineering Journal*. 415 (2021) 128188.
- [6] D.R. Kumar, K.R. Prakasha, A.S. Prakash, J.-J. Shim, Direct growth of honeycomb-like NiCo₂O₄@Ni foam electrode for pouch-type high-performance asymmetric supercapacitor, *Journal of Alloys and Compounds*. 836 (2020) 155370. doi:10.1016/j.jallcom.2020.155370.
- [7] L. Liu, H. Zhao, Y. Lei, Review on nanoarchitected current collectors for pseudocapacitors, *Small Methods*. 3 (2019) 1800341.
- [8] A. Ehsani, A.A. Heidari, H.M. Shiri, Electrochemical pseudocapacitors based on ternary nanocomposite of conductive polymer/graphene/metal oxide: An introduction and review to it in recent studies, *The Chemical Record*. 19 (2019) 908-926.
- [9] M.-Y. Chung, C.-T. Lo, High-performance binder-free RuO₂/electrospun carbon fiber for supercapacitor electrodes, *Electrochimica Acta*. 364 (2020) 137324.
- [10] Y. Kumar, S. Chopra, A. Gupta, Y. Kumar, S.J. Uke, S.P. Mardikar, Low temperature synthesis of MnO₂ nanostructures for supercapacitor application, *Materials Science for Energy Technologies*. 3 (2020) 566-574.
- [11] H. Xing, G. Long, J. Zheng, H. Zhao, Y. Zong, X. Li, Y. Wang, X. Zhu, M. Zhang, X. Zheng, Interface engineering boosts electrochemical performance by fabricating CeO₂@CoP Schottky junction for hybrid supercapacitors, *Electrochimica Acta*. 337 (2020) 135817.
- [12] S. Cheng, Y. Zhang, Y. Liu, Z. Sun, P. Cui, J. Zhang, X. Hua, Q. Su, J. Fu, E. Xie, Energizing Fe₂O₃-based supercapacitors with tunable surface pseudocapacitance via physical spatial-confining strategy, *Chemical Engineering Journal*. 406 (2021) 126875.
- [13] C. Liu, Q. Li, Q. Zhang, B. He, P. Man, Z. Zhou, C. Li, L. Xie, Y. Yao, Surface-functionalized Fe₂O₃ nanowire arrays with enhanced pseudocapacitive performance as novel anode materials for high-energy-density fiber-shaped

- asymmetric supercapacitors, *Electrochimica Acta*. 330 (2020) 135247.
- [14] D. Chen, D. Pang, S. Zhang, H. Song, W. Zhu, J. Zhu, Synergistic coupling of NiCo₂O₄ nanorods onto porous Co₃O₄ nanosheet surface for tri-functional glucose, hydrogen-peroxide sensors and supercapacitor, *Electrochimica Acta*. 330 (2020) 135326. doi:10.1016/j.electacta.2019.135326.
- [15] G.M. Tomboc, H. Kim, Derivation of both EDLC and pseudocapacitance characteristics based on synergistic mixture of NiCo₂O₄ and hollow carbon nanofiber: An efficient electrode towards high energy density supercapacitor, *Electrochimica Acta*. 318 (2019) 392-404. doi:10.1016/j.electacta.2019.06.112.
- [16] H. Wang, Y. Zhong, J. Ning, Y. Hu, Recent advances in the synthesis of non-carbon two-dimensional electrode materials for the aqueous electrolyte-based supercapacitors, *Chinese Chemical Letters*. (2021). doi:10.1016/j.ccllet.2021.04.025.
- [17] M.A.A. Mohd Abdah, N.H.N. Azman, S. Kulandaivalu, Y. Sulaiman, Review of the use of transition-metal-oxide and conducting polymer-based fibres for high-performance supercapacitors, *Materials & Design*. 186 (2020) 108199. https://doi.org/10.1016/j.matdes.2019.108199.
- [18] M. Bigdeloo, E. Kowsari, A. Ehsani, A. Chinnappan, S. Ramakrishna, R. AliAkbari, Review on innovative sustainable nanomaterials to enhance the performance of supercapacitors, *Journal of Energy Storage*. 37 (2021) 102474. doi:10.1016/j.est.2021.102474.
- [19] S.A. Delbari, L.S. Ghadimi, R. Hadi, S. Farhoudian, M. Nedaei, A. Babapoor, A. Sabahi Namini, Q.V. Le, M. Shokouhimehr, M. Shahedi Asl, M. Mohammadi, Transition metal oxide-based electrode materials for flexible supercapacitors: A review, *Journal of Alloys and Compounds*. 857 (2021) 158281. doi:10.1016/j.jallcom.2020.158281.
- [20] G. Yang, S.-J. Park, Facile hydrothermal synthesis of NiCo₂O₄-decorated filter carbon as electrodes for high performance asymmetric supercapacitors, *Electrochimica Acta*. 285 (2018) 405-414. doi:10.1016/j.electacta.2018.08.013.
- [21] D.P. Dubal, J.G. Kim, Y. Kim, R. Holze, C.D. Lokhande, W.B. Kim, Supercapacitors based on flexible substrates: an overview, *Energy Technology*. 2 (2014) 325-341.
- [22] P. Siwatch, K. Sharma, S.K. Tripathi, Facile synthesis of NiCo₂O₄ quantum dots for asymmetric supercapacitor, *Electrochimica Acta*. 329 (2020) 135084. doi:10.1016/j.electacta.2019.135084.
- [23] Z. Lu, D. Xuan, D. Wang, J. Liu, Z. Wang, Q. Liu, D. Wang, Y.-Y. Ye, Z. Zheng, S. Li, Reagents-assisted hydrothermal synthesis of NiCo₂O₄ nanomaterial as electrode for high-performance asymmetric supercapacitor, *New J. Chem.* (2021). doi:10.1039/D1NJ00268F.
- [24] G. Yang, S.-J. Park, Nanoflower-like NiCo₂O₄ grown on biomass carbon coated nickel foam for asymmetric supercapacitor, *Journal of Alloys and Compounds*. 835 (2020) 155270. doi:10.1016/j.jallcom.2020.155270.
- [25] Y. Li, L. Zheng, W. Wang, Y. Wen, Controllable Synthesis of NiCo₂O₄/CNT Composites for Supercapacitor Electrode Materials, *Int. J. Electrochem. Sci.* 15 (2020) 11567-11583.
- [26] B. Asbani, K. Robert, P. Roussel, T. Brousse, C. Lethien, Asymmetric micro-supercapacitors based on electrodeposited RuO₂ and sputtered VN films, *Energy Storage Materials*. 37 (2021) 207-214.

- [27] N. Yadav, S.A. Hashmi, Hierarchical porous carbon derived from eucalyptus-bark as a sustainable electrode for high-performance solid-state supercapacitors, *Sustainable Energy & Fuels*. 4 (2020) 1730-1746.
- [28] M. Pathak, J.R. Jose, B. Chakraborty, C.S. Rout, High performance supercapacitor electrodes based on spinel NiCo₂O₄@ MWCNT composite with insights from density functional theory simulations, *The Journal of Chemical Physics*. 152 (2020) 064706.
- [29] M. Eskandari, R. Malekfar, D. Buceta, P. Taboada, NiCo₂O₄-based nanostructured composites for high-performance pseudocapacitor electrodes, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 584 (2020) 124039. doi:10.1016/j.colsurfa.2019.124039.
- [30] S.J. Uke, G.N. Chaudhari, A.B. Bodade, S.P. Mardikar, Morphology dependant electrochemical performance of hydrothermally synthesized NiCo₂O₄ nanomorphs, *Materials Science for Energy Technologies*. 3 (2020) 289-298.
- [31] NiCo₂O₄-based nanostructured composites for high-performance pseudocapacitor electrodes, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 584 (2020) 124039. doi:10.1016/j.colsurfa.2019.124039.
- [32] S.J. Uke, V.P. Akhare, S.P. Meshram, G.N. Chaudhari, Triethanol amine ethoxylate (TEA-EO) driven controlled synthesis of NiCo₂O₄ nanostructures, their characterization and supercapacitor performance, *Advanced Science, Engineering and Medicine*. 10 (2018) 1174-1182.
- [33] D. Guragain, C. Zequine, T. Poudel, D. Neupane, R.K. Gupta, S.R. Mishra, Influence of urea on the synthesis of NiCo₂O₄ nanostructure: morphological and electrochemical studies, *Journal of Nanoscience and Nanotechnology*. 20 (2020) 2526-2537.
- [34] W.D. Wang, P.P. Zhang, S.Q. Gao, B.Q. Wang, X.C. Wang, M. Li, F. Liu, J.P. Cheng, Core-shell nanowires of NiCo₂O₄@ α -Co(OH)₂ on Ni foam with enhanced performances for supercapacitors, *Journal of Colloid and Interface Science*. 579 (2020) 71-81. doi:10.1016/j.jcis.2020.06.048.
- [35] H. Yang, C. Zeng, C. Sun, M. Wang, Y. Gao, Mesopores NiCo₂O₄ nano-needles directly grown on Ni foam as high-performance electrodes for supercapacitors, *Materials Letters*. 279 (2020) 128523. doi:10.1016/j.matlet.2020.128523.
- [36] F. Ren, Z. Tong, S. Tan, J. Yao, L. Pei, A. Abulizi, Ultrathin and porous NiCo₂O₄ nanosheets based 3D hierarchical electrode materials for high-performance asymmetric supercapacitor, *Journal of Electrochemical Energy Conversion and Storage*. (2021) 1-11.
- [37] Y. Li, Z. Zhang, Y. Chen, H. Chen, Y. Fan, Y. Li, D. Cui, C. Xue, Facile synthesis of a Ni-based NiCo₂O₄-PANI composite for ultrahigh specific capacitance, *Applied Surface Science*. 506 (2020) 144646. doi:10.1016/j.apsusc.2019.144646.
- [38] Z. Cao, C. Liu, Y. Huang, Y. Gao, Y. Wang, Z. Li, Y. Yan, M. Zhang, Oxygen-vacancy-rich NiCo₂O₄ nanoneedles electrode with poor crystallinity for high energy density all-solid-state symmetric supercapacitors, *Journal of Power Sources*. 449 (2020) 227571. doi:10.1016/j.jpowsour.2019.227571.
- [39] R. Bai, X. Luo, D. Zhen, C. Ci, J. Zhang, D. Wu, M. Cao, Y. Liu, Facile fabrication of comb-like porous NiCo₂O₄ nanoneedles on Ni foam as an advanced electrode for high-performance supercapacitor, *International Journal of Hydrogen*

Energy. 45 (2020) 32343-32354.
doi:10.1016/j.ijhydene.2020.08.156.

[40] S.S. Jayaseelan, S. Radhakrishnan, B. Saravanakumar, M.-K. Seo, M.-S. Khil, H.-Y. Kim, B.-S. Kim, Mesoporous 3D NiCo₂O₄/MWCNT nanocomposite aerogels prepared by a supercritical CO₂ drying method for high performance hybrid supercapacitor electrodes, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 538 (2018) 451-459.
doi:10.1016/j.colsurfa.2017.11.037.

[41] Preparation of Ordered Mesoporous Carbon/NiCo₂O₄ Electrode and It...: Ingenta Connect, (n.d.). <https://www.ingentaconnect.com/content/apcs/apcs/2012/00000028/00000004/art00016#> (accessed April 26, 2021).

[42] C. Young, R. Salunkhe, S. Alshehri, T. Ahamad, Z. Huang, J. Henzie, Y. Yamauchi, High Energy Density Supercapacitors Composed of Nickel Cobalt Oxide Nanosheets on Nanoporous Carbon Nanoarchitectures, *Journal of Materials Chemistry A*. 5 (2017). doi:10.1039/C7TA01362K.

[43] N.V. Nguyen, T.V. Tran, S.T. Luong, T.M. Pham, K.V. Nguyen, T.D. Vu, H.S. Nguyen, N.V. To, Facile Synthesis of a NiCo₂O₄ Nanoparticles Mesoporous Carbon Composite as Electrode Materials for Supercapacitor, *ChemistrySelect*. 5 (2020) 7060-7068.

[44] J. Fang, C. Kang, L. Fu, S. Li, Q. Liu, Fabrication of hollow bamboo-shaped NiCo₂O₄ with controllable shell morphologies for high performance hybrid supercapacitors, *Journal of Alloys and Compounds*. 849 (2020) 156317. doi:10.1016/j.jallcom.2020.156317.

[45] P. Siwatch, K. Sharma, N. Singh, N. Manyani, S.K. Tripathi, Enhanced supercapacitive performance of reduced graphene oxide by incorporating NiCo₂O₄ quantum dots using aqueous

electrolyte, *Electrochimica Acta*. 381 (2021) 138235. doi:10.1016/j.electacta.2021.138235.

[46] L. Hou, W. Yang, X. Xu, B. Deng, J. Tian, S. Wang, F. Yang, Y. Li, In-situ formation of oxygen-vacancy-rich NiCo₂O₄/nitrogen-deficient graphitic carbon nitride hybrids for high-performance supercapacitors, *Electrochimica Acta*. 340 (2020) 135996. doi:10.1016/j.electacta.2020.135996.

[47] J. Chen, T. Ma, M. Chen, Z. Peng, Z. Feng, C. Pan, H. Zou, W. Yang, S. Chen, Porous NiCo₂O₄@Ppy core-shell nanowire arrays covered on carbon cloth for flexible all-solid-state hybrid supercapacitors, *Journal of Energy Storage*. 32 (2020) 101895. doi:10.1016/j.est.2020.101895.

[48] M. Chatterjee, S. Saha, S. Das, S.K. Pradhan, Advanced asymmetric supercapacitor with NiCo₂O₄ nanoparticles and nanowires electrodes: A comparative morphological hierarchy, *Journal of Alloys and Compounds*. 821 (2020) 153503. doi:10.1016/j.jallcom.2019.153503.

[49] P. Salarizadeh, M.B. Askari, M. Seifi, S.M. Rozati, S.S. Eisazadeh, Pristine NiCo₂O₄ nanorods loaded rGO electrode as a remarkable electrode material for asymmetric supercapacitors, *Materials Science in Semiconductor Processing*. 114 (2020) 105078. doi:10.1016/j.mssp.2020.105078.

[50] Z. Wei, J. Guo, M. Qu, Z. Guo, H. Zhang, Honeycombed-like nanosheet array composite NiCo₂O₄/rGO for efficient methanol electrooxidation and supercapacitors, *Electrochimica Acta*. 362 (2020) 137145. doi:10.1016/j.electacta.2020.137145.