Transition metal oxides/hydroxides nanoarrays for aqueous electrochemical energy storage systems

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The need for the development of efficient electrochemical energy storage devices with high energy density, power density and safety is becoming more and more urgent in recent years, and the key for achieving the outstanding performance is the suitable structural designing of active materials. Nanoarray architecture emerged as one of the most promising structures, as it can offer many advantages to boost the electrochemical performance. Specifically, this kind of integrated electrodes can provide a large electrochemically active surface area, faster electron transport and electrolyte ion diffusion, leading to substantially improved capacitive, rate and cycling performances. In this paper, we will review the recent advances in strategies for synthesis of materials with nanoarray architectures and their applications in supercapacitors and batteries.

INTRODUCTION

Energy is one of the most important topics in the 21st century. With the rapid depletion of fossil fuels and increasingly worsened environmental pollution caused by vast fossil-fuel consumption, it is highly demanded to make more efficient use of energy while seeking renewable and clean energy sources to enable the sustainable development of our society [1]. Developing advanced energy storage systems with high energy density, high power density and prominent cycling stability is one of the most effective ways for increasing the efficiency. Ellis *et al.* [2] have provided a comparison of the characteristics of several common energy storage devices, as shown in Fig. 1. Fuel cells and batteries usually possess higher energy density, while capacitors and electrochemical supercapacitors (SCs) deliver higher power density with a short response time [2,3]. As two important devices for electrochemical energy storage (EES), batteries and SCs have attracted a worldwide attention and realized wide practical application as power sources for portable electronics such as cell phones and laptops and have great potentials to completely power electric vehicles and to be used in large-scale electrical grids [4,5]. For safety concerns, aqueous supercapacitors and batteries are definitely more favorable because of the nonflammability of the electrolyte.

These two major charge storage systems (aqueous SCs and batteries) are different in energy storage and conversion mechanisms. SCs can essentially be classified into two types: electric double layer capacitors (EDLCs) and pseudocapacitors (PCs). The former storage mode is an electrostatic (physical) process with fast charge adsorption and separation at the interface between electrode and electrolyte. The latter is a chemical process involving redox reactions between electrode materials and electrolyte ions [1,6]. As a result, EDLCs can provide higher power densities but inferior energy densities, while PCs possess much higher energy densities with compromised power densities. These two types of SCs can be easily distinguished by either cyclic voltammograms (CV) or galvanostatic discharge (GD) behavior (shown in Fig. 2). For EDLCs, the CV curve is close to a classic rectangular shape and the GD curve is almost linear, while the CV curve is characterized by faradaic redox peaks and there are one or multiple platforms in GD curve for PCs [7]. For batteries, the shapes of CV and GD curves are quite similar to those of PCs.

Developing advanced electrodes with novel approaches and structures are critical for improving such electrochemical energy storage systems. In traditional process of lithium ion battery industry, the active material powder is painted on the metallic foil with the assistance of binder [8]. How-

Figure 1 A Ragone plot of various energy storage devices. Reprinted with permission from Ref. [2] (Copyright 2014, Wiley-VCH).

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Figure 2 The electrochemical characteristics for distinguishing EDLCs and PCs. The CV curves of (a) EDLCs and (b) PCs; the GD curves of (c) EDLCs and (d) PCs. Reprinted with permission from Ref. [7] (Copyright 2014, AAAS).

ever, the loose contact between the materials and substrates will compromise the rate and cycling performances. Constructing the materials into nanoarray architectures, that is, some geometrically confined structures built with one dimensional (1D) or two dimensional (2D) primary nanostructures, which have similar dimension and size with similar orientations, has been proved effective to overcome the above problem [9–13]. In addition, these nanoarrays often exhibit fascinating properties, which are desirable for EES electrodes. It could provide large surface area and tunable free spaces for volume expansion, prevent agglomeration, facilitate the electron transfer rate and the penetration of the electrolytes into the whole electrode matrix, and strengthen the connection between active materials and substrates [2,14–17]. A schematic representation of an idealized nanoarrays electrode is shown in Fig. 3.

A lot of excellent reviews have reported various EES systems, which focus on different electrolyte types including organic electrolytes, aqueous phase and ionic liquids [1–5,14]. Here in this paper we will summarize several fabrication processes of metal oxide and hydroxide materials with

Figure 3 Schematic representation of a typical nanoarray.

nanoarray architectures as well as their applications mainly in aqueous media. As well known, transition metal oxides and hydroxides are considered as the promising materials for next generation aqueous EES devices, owing to their multiple oxidation states that enable rich redox reactions for pseudocapacitance generation [18–20], while designing the electrochemically active materials into ordered nanoarrays architectures has been demonstrated effective for achieving higher performance. Thereby we would focus on the recent advances of nanoarray materials as high-performance electrodes for aqueous EES systems including SCs and batteries. At the last section, we put forward several possible research trends in the electrode architecture design to further improve the EES performance which may greatly outperform the state-of-art energy storage devices.

SUBSTRATES AND SYNTHETIC METHODS

First of all, it should be pointed out that one electrode is constructed with a current collector and active materials loaded on it. Thus, both the choice on current collector (or substrate) and the loading method will significantly determine the performance of final electrodes for given electrochemically active materials.

The substrate is a very important part for an electrode, especially for nanoarray based materials. It acts as not only a current conductor but also a template to grow ordered arrays. The crystal structure and the orientation of the substrates often play a vital role in the growth process of arrays [15]. Thus, the choice of the substrate will significantly affect the overall performance of the nanoarray materials.

The traditional substrate usually has a planar surface [20], which largely limits the contact area and the loading mass of the active materials. For this concern, 3D porous structures are more desirable to achieve larger surface area and high mass-loading. As an evolution of current collector, Ni foam is now widely used as the substrate, due to the large and uniform macropores, large supporting area and high electrical conductivity [21]. As we have estimated, for one piece of Ni foam (0.5 mm in thickness and 30 mg cm⁻² in weight, assuming the diameter of all primary microwires constructing the networks are 10 μm in diameter), 30 cm² of specific surface area can be achieved per 1 cm² Ni foam, due to the existence of pores with tens of micrometers in size.

The most obvious drawback of Ni foam is its instability in acid environment, which will dissolve the Ni foam and destroy the whole structure [22]. Thus, the Ni foam can only be used as substrate or current collector in neutral or alkali environments. Another issue is the pseudocapacitive contribution of the Ni foam surface, which might interfere the capacitance calculation, but as we have calculated, if the mass-loadings of the active materials are high enough

to achieve a large areal capacitance (e.g. $>4 \text{ F cm}^{-2}$), the inevitable substrate contribution ($\sim 0.2 \text{ F cm}^{-2}$) can be neglected [23]. In a word, Ni foam is a good current collector in alkaline or neutral electrodes as long as we subtract the possible capacitive contribution to get corrected specific capacitances of the active material [24]. As an alternative option of Ni foam, Cu foam has been used widely because of its high resistance to acidity and negligible capacitive contribution [25,26].

The aforementioned substrates usually suffer from their high weights, which contribute a considerable proportion of the total weight of EES devices. Nevertheless, if heavy current collectors can be replaced by more lightweight materials, the effective SC for an entire capacitor device can be further improved [8,27]. Carbon materials are the most widely-used lightweight current collector for EES, such as carbon cloth [28], carbon fiber [29] and graphite foams [30], which have been prepared and indeed performed excellently as long as the carbon-oxide interface is constructed.

Some specific applications prompt interests on other specially designed electrodes. For instance, transparent electrode is a necessary component in many modern devices such as touch screens, LCDs, OLEDs, and solar cells [31–33]. The most common transparent substrates are tin and fluorine doped indium oxide (ITO and FTO), which possess the advantages of innate transparency ($\sim 90\%$ in visible region), high electrical conductivity ($\sim 10^4 \text{ S cm}^{-1}$), and chemical inertness [34]. However, They have certain problems, mainly centered on their scarcity of supply, and the ceramic nature [35]. Very recently, transparent electrodes based on metal nanowires [33] have been widely investigated, but their practicability needs further demonstration.

Every substrate has its corresponding loading method. As we mentioned before, the traditional method of preparing electrodes is painting the powder onto the current collector with assistance of binder. Compared to that, direct deposition or growth of electrochemically active materials onto conductive substrate is obviously more effective for achieving intimate contact between the current collector and the energy storage material. It is usually organized by electrochemical/hydrothermal transformation technique with or without the assistance of templates [36]. Common templates include anodized aluminium oxide (AAO) [37], anodized TiO_2 nanotubes [38], ZnO nanorod template [39] and some track-etched polymer templates [40].

It should be noted that hybrid nanoarrays can also be constructed by some template-free electrochemical methods, which is more facile, cost-effective and environmental friendly. Commonly chemical vapor deposition (CVD) [41] is used for controllable fabrication of highly ordered nanostructure on substrate by gas-solid reaction, while

chemical bath deposition and hydrothermal method [42, 43] are two typical wet means. Some examples including large area MnO_2 nanowire (70–100 nm in diameter and 1.5 μm in length) arrays grown on fluorine-doped tin oxide coated glass [44], mesoporous (2–5 nm in pore-size) NiCo_2O_4 nanosheets loading on Ni foam [21], and porous (10–200 nm in diameters) Ni/Co(OH)_2 nanoflake films (20 nm in thickness) by a two-step electrodeposition process on Ni foam [45] have been reported.

Hydrothermal synthetic strategies on aqueous systems are considered as simple and powerful routes and recently become more and more popular in fabricating ordered nanoarray structures. This method relies on the chemical reactions and solubility changes of substances in a sealed heated aqueous solution above ambient temperature and pressure to grow nanocrystals [19]. The nucleation process on the surface of substrate is quite slow, which avoids the mixed and disorderly arrangement. The hydrothermal method has many advantages: i) this route is very versatile because the hydrothermal process occurs on a variety of materials, such as Ni(OH)_2 [46], MnO_2 [47], Co(OH)_2 [22,48], FeOOH [49], Cu(OH)_2 [50], ZnO [51], V_2O_5 [52]; ii) the reaction parameters can be easily controlled including temperature, time and concentration, which would result in different morphologies, porosity and compositions of the final products [19,53]; iii) multiple hydrothermal processes can be employed to grow hierarchical nanoarray structures with different components ($\text{Co}_3\text{O}_4@\text{NiO}$ [42,43], TiO_2 [54], $\text{Ni}_3\text{S}_2@\text{MoS}_2$ [55], $\text{Co}_3\text{O}_4@\text{MnO}_2$ [56], ZnO [57], $\text{Co}_3\text{O}_4@\text{Fe}_2\text{O}_3$ [58]), which offer an even higher porosity and mass-loading of the active layer.

STRUCTURAL ADVANTAGE OF NANOARRAY MATERIALS AS EES ELECTRODES

Carbon nanoarrays for electrodes

Carbon materials are regarded as the most promising electrode materials for industrialization. The energy storage mechanism of carbon materials belongs to the EDLCs, which is mainly originated from the accumulation of electric charges across the electrode/electrolyte interface [59,60]. The most important factors influencing their electrochemical performance are the specific surface area and pore-size distribution [14,61,62]. The usual form of ordered carbon-based nanoarray materials is carbon nanotube arrays (CNTAs) [63] which possess highly-ordered pore structures and high effective specific surface area. The ideal illustration of the CNTAs is shown in Fig. 4. The conductive channels and the one-dimensional structures in the CNTAs facilitate the ion and electron transportation and provide improved charge storage/deliver properties, which are highly desirable for high-rate applications [64,65]. Lat-

Figure 4 Ideal illustration of the CNTAs direct grown on current collector. Reprinted with permission from Ref. [4] (Copyright 2008, Nature Publishing Group).

est report also demonstrated that highly porous graphene film could also be constructed by template-dependent method and showed promising performance for SCs [66]. In order to improve the specific capacitance of the CNTAs, researchers introduced pseudocapacitive materials which possessed much higher capacitances into the 3D network [63]. Fan *et al.* [41] reported a novel strategy to prepare 3D CNTA-graphene sandwich (CGS) structures with CNTAs grown in between the graphene layers by co-catalyst CVD approach. The SC based on CGS exhibits a specific capacitance of 385 F g^{-1} , much higher than that of the counterpart.

Pseudocapacitive nanoarray materials for electrodes

One dimensional nanoarray materials

One dimensional (1D) structured nanoarrays, including nanowires, nanorods and nanotubes are the basic structures in nanoarrays [15,67]. The 1D nanostructure can offer a direct pathway for electron transfer and the high aspect ratio can facilitate the electrolyte penetration and

maximize the utilization of the active materials [19,68].

Our group has employed a facile hydrothermal reaction followed by a calcination process to fabricate NiO nanorod arrays [69], which showed a combination of ultrahigh specific capacitance, high power density and good cycling stability. As schemed in Fig. 5, the slim rod morphology reduced the diffusion distance through which the electrolyte had to penetrate to less than 10 nm [70], and thereby increasing the active surface area for insertion and extrusion of OH^- and consequently maximizing the pseudocapacitance (Zone 1). Concurrently it also maximized the surface area exposed to the bulk solution, which enlarged the EDLC, as shown in the discharge curves (Zone 2). As a result, the measured capacitance was as high as 2018 F g^{-1} , close to the theoretical value (2573 F g^{-1}).

Lu *et al.* [44] have studied the effect of different structures on the electrochemical performance. They synthesized large-area MnO_2 nanorod arrays (MONRAs) and herringbones (MOHBs) on FTO substrates by similar electrochemical methods. Although the MOHBs showed a larger surface area than the MONRAs, the MONRAs showed a better capacitive performance, indicating that vertically aligned nanorod array was more desirable because of the high electron transport rate, as shown in Fig. 6.

Two dimensional nanoarray materials

Two-dimensional (2D) nanostructures, typically nanosheet, usually possess a thin thickness nature, thus inheriting the advantages of slim 1D nanostructures. Compared with 1D nanoarray, the active surface area of ultrathin 2D nanoarray materials is smaller, but the contact area of the materials to the substrate is much larger, which leads to better electrical contact (shown in Fig. 7), thus beneficial for the electron transport and rate capability. Besides, the larger size of 2D nanostructure offers a higher loaded mass on

Figure 5 A schematic image showing how the NiO nanorod generates EDLC and pseudocapacitance. Reprinted with permission from Ref. [69] (Copyright 2011, Springer).

Figure 6 Schematic representation of the electron path on (a) MONRAs and (b) MOHBs electrodes. Reprinted with permission from Ref. [44] (Copyright 2011, The Royal Society of Chemistry).

Figure 7 The schematic of 1D and 2D nanomaterials.

geometric area, which is beneficial to improve the areal capacitance [71].

Our group has developed a facile hydrothermal route to fabricate an ultrathin $\text{Ni}(\text{OH})_2$ nanowalls film on Ni foam [46]. It is found that the extremely thin thickness (~ 6 nm) of the nanowalls played an important role in yielding the ultrahigh capacitance by effectively shortening the proton diffusion distance and making the chemically active materials almost 100% usable for redox reaction. Meanwhile, it also provided additional EDLC at the interfaces, which endowed the $\text{Ni}(\text{OH})_2$ nanowalls with an ultrahigh capacitance of $2,675 \text{ F g}^{-1}$ (7.85 F cm^{-2}) and 96%–98% retention depending on the varied current density. Yuan *et al.* [72] and Zhao *et al.* [73] also found that Co_3O_4 and MnO_2 with ultrathin nanosheet structures could also deliver ultrahigh capacitive performances, demonstrating the effectiveness of this structural design.

Layered double hydroxides (LDHs), which have a general formula of $[\text{M}_{1-x}^{2+}\text{M}_x^{3+}(\text{OH})_2]^{x+}[\text{A}_{x/n}^{n-}\cdot m\text{H}_2\text{O}]^{x-}$ (M^{2+} and M^{3+} , the bivalent and trivalent metal cations, respectively; A^{n-} , the charge-balancing anion of valence; $x = \text{M}^{3+}/(\text{M}^{2+} + \text{M}^{3+})$), have attracted increasing interest from both academic and industrial angles due to their wide applications in various areas [74]. Recently, LDHs with vertically aligned structures have exhibited great potential in SCs [75–78]. Gu *et al.* [79] prepared a NiTi-LDH nanosheet film by a two-step hydrothermal process, which showed a high areal capacitance of 10.37 F cm^{-2} at 5 mA cm^{-2} . To further improve the EES performance of 2D structure, creating holes in the nanosheets to increase the porosity is regarded as an effective method. Our group has fabricated

a thin mesoporous cobalt carbonate hydroxide (MPCCH) nanosheet array by selectively etching the Al element of a CoAl-LDH thin film in highly concentrated NaOH solution [80]. The specific capacitance of the MPCCH could reach $1,075 \text{ F g}^{-1}$ at 5 mA cm^{-2} , which was much higher than that of the CoAl-LDH precursor. Further studies also confirmed the effectiveness of this structural design for LDHs. Chen *et al.* [81] have grown NiCo-LDH films on Ni foam with ultrathin nanosheets and porous nanostructures, which displayed a significantly enhanced specific capacitance ($2,682 \text{ F g}^{-1}$ at 3 A g^{-1}). The possible formation mechanism of NiCo LDH is shown in Fig. 8.

Hierarchical nanoarray materials

For practical application of SCs, high areal capacitance of EES electrode is actively pursued, which requires a combination of high mass-loading and high utilization of electrochemically active material. In general, high mass-loading on conventional electrodes usually leads to an increase of “dead volume” in electrode materials which is not accessible to the electrolyte in the SC, and thus results in low utilization efficiencies of the materials. In this regard, hierarchical design of complex core-shell nanoarrays with porous structures is considered as an effective approach to simultaneously achieve high mass-loading and high utilization of the electrode material, because they not only provide large active surface area and short diffusion path lengths to electrons and ions, but also show a potential synergistic effect of each component, leading to high capacitance, low internal resistance, remarkable rate capability, and excellent stability [5,24,82–86].

According to the aforementioned advantages of hierarchical structure design, our team has synthesized 3D $\text{Co}_3\text{O}_4@\text{Co}_3\text{O}_4$ and $\text{Co}_3\text{O}_4@\text{NiO}$ hierarchical nanoarrays electrodes for SC [42,43,53]. Thanks to the unique architecture, these hierarchical nanoarray electrodes showed excellent electrochemical performance, much better than the individual components (Co_3O_4 nanosheet arrays and

Figure 8 The possible formation mechanism of NiCo LDH hybrid films supported on Ni foam and the illustration scheme of the asymmetrical SCs. Reprinted with permission from Ref. [81] (Copyright 2014, WILEY-VCH).

Table 1 Comparison of the capacity, mass loading and capacity retention of hierarchical structural nanoarray materials

Materials	Specific capacitance (F g ⁻¹)	Areal capacitance (F cm ⁻²)	Mass loading (mg cm ⁻²)	Capacitance retention
Co ₃ O ₄ @Ni-Co-O [42]	2098 (5 mA cm ⁻²)	24.95	12	96% (1000 cycles)
Co ₃ O ₄ @NiO [43]	2033 (5 mA cm ⁻²)	39.6	19.5	~100% (1000 cycles)
Hierarchical Co ₃ O ₄ [53]	715 (5 mA cm ⁻²)	5.44	7.6	~100% (1000 cycles)
Ni ₃ S ₂ @Ni(OH) ₂ [83]	1277 (2 mV s ⁻¹)	4.7	3.7	99.1% (2000 cycles)
CoO@Ni(OH) ₂ [82]	798 (1.67 A g ⁻¹)	2.7	3.4	95% (2000 cycles)
Co ₃ O ₄ @MnO ₂ [87]	480 (2.67 A g ⁻¹)	0.56	1.2	97.3% (5000 cycles)
NiCo ₂ O ₄ @MnO ₂ [88]	1471 (10 mA cm ⁻²)	2.06	1.4	88% (2000 cycles)
Co ₃ O ₄ @NiO [24]	853 (2 A g ⁻¹)	2.56	3	95% (6000 cycles)
SnO ₂ /MnO ₂ [89]	800 (1 A g ⁻¹)			83% (2500 cycles)
NiCo ₂ O ₄ [90]	1118 (5.6 mA cm ⁻²)	3.12	3	89% (2000 cycles)

nanowire arrays). The ultrahigh mass loading (12–20 mg cm⁻²) and thin morphologies of the electrode result in an ultrahigh areal capacitances up to ~40 F cm⁻², which is the highest among the reported values (Table 1), while the rate capability and cycling stability are well preserved.

This architecture design is also applicable for other pseudocapacitive materials. Liu *et al.* [87] have used 3D ordered amorphous carbon layers function as a sacrificial reactive template to anchor MnO₂ nanostructures onto another metal oxide scaffolds, producing hierarchical hybrid nanostructure arrays for SC applications. The purposely built smart electrode made of a Co₃O₄@MnO₂ nanowire array exhibits excellent electrochemical performance, much better than the individual parts. Mai *et al.* [91] also synthesized 3D multicomponent oxides, MnMoO₄/CoMoO₄ with high capacitance. Liu *et al.* [92] reported the synthesis of MnO₂-NiO nanoflake-assembled tubular array on stainless steel substrate to function as pseudocapacitor electrode, which displays an areal capacitance that is four orders of magnitude higher than that of carbonaceous materials.

APPLICATIONS OF NANOARRAY MATERIALS IN EES SYSTEMS

A total EES system usually consists of two electrodes, an electrolyte, and a separator that electrically isolates the two electrodes [14]. In this section, we will review the applications of nanoarray materials in some common systems including symmetric supercapacitors (SSCs), asymmetric supercapacitors (ASCs) and batteries, and firstly we will define some terminologies as following.

The total capacitance (C_T) of the EES system can be calculated as Equation (1):

$$\frac{1}{C_T} = \frac{1}{C_P} + \frac{1}{C_N}, \quad (1)$$

where C_P and C_N are the capacitance of the positive and negative electrodes based on a three-electrode setup, respectively. For SCs, if the two electrodes are identical ($C_P = C_N$), the corresponding system is called a SSC and the total

capacitance C_T will be one half of either one's capacitance. In other case, the positive and negative electrodes use different materials corresponding to ASCs, and C_T will depend on the relatively small value between C_P and C_N [64].

Energy and power densities are two crucial parameters for evaluating the electrochemical performance of SCs. The maximum energy (E) and power densities (P) of a SC can be obtained using Equations (2) and (3), respectively [14,59]:

$$E = \frac{1}{2} C_T V^2, \quad (2)$$

$$P = \frac{V^2}{4R}, \quad (3)$$

where C_T is the total capacitance of the system; V is the operating voltage, which is determined by the thermodynamic stability of an electrolyte and dependent upon the electrode materials; and R is the equivalent series resistance. Therefore, in order to achieve excellent performance for a SC, it is of critical significance to find two SC electrodes with matched capacitances and simultaneously possess high capacitance, wide operating cell voltage, and minimum equivalent series resistance.

Coupling nanoarray materials for SSCs

The SSC is a common type in conventional EES system, which includes two same electrodes. The material screening is of great importance to assemble SSCs because the materials should be active in a wide range of potential. Up to now, only several materials have been successfully applied in SSCs, such as carbon [93], MnO₂ [94] and RuO₂ [95]. Since the scarcity and high cost of RuO₂, carbon and manganese oxides have been widely investigated as cheap alternatives [96]. Reddy *et al.* [94] have assembled a SSC involving two Au-MnO₂/CNT electrodes, delivering high energy density and remarkable rate capability.

Design of ASCs

Assembling ASCs have been found to be an effective ap-

proach to increase the energy density of SCs. The ASCs usually consist of two different-type electrodes, simultaneously offering the advantages of both SCs (rate, cycle life) and advanced batteries (energy density) [97]. Therefore, ASCs can make full use of the different potential windows of the two electrodes to provide a maximum operation voltage in the cell system, accordingly resulting in a greatly enhanced specific capacitance and significantly improved energy density [47,98,99].

Materials with redox potentials above 0 V (vs. normal hydrogen electrode) can be considered as positive materials, such as MnO_2 , Co_3O_4 and $\text{Ni}(\text{OH})_2$, as we have mentioned in the previous section. With regard to the negative materials, carbonaceous materials such as porous carbons, CNTs and graphene often act as electrodes with the working potential window below 0 V for ASCs [100]. Wu *et al.* [97] developed a high-voltage ASC based on graphene as negative electrode and a MnO_2 nanowire/graphene composite (MGC) as positive electrode in a neutral aqueous Na_2SO_4 solution as electrolyte. This ASC can be cycled reversibly in the high voltage region of 0–2.0 V and exhibits a superior energy density of 30.4 W h kg^{-1} . Zhou *et al.* [101] fabricated an ASC by using 3D CoO@Polypyrrole nanowires array as the positive electrode and activated carbon (AC) film as the negative electrode. This device has demonstrated high energy density of 43.5 W h kg^{-1} and outstanding cycling stability.

Nanoarray materials for aqueous rechargeable batteries

Different from ASCs, aqueous batteries consist two electrodes both with battery-type faradaic character. Hundreds of electrochemical redox couples have been proposed to construct rechargeable batteries [102,103]. Fig. 9 summarizes the working potential windows of various pseudocapacitive materials in aqueous electrolyte [104], demonstrating that materials such as $\text{Ni}(\text{OH})_2$, MnO_2 and Co_3O_4

Figure 9 The working potential windows of various pseudocapacitive type materials in aqueous electrolyte. Reprinted with permission from Ref. [104] (Copyright 2011, Wiley-VCH).

can be used as cathodes while Bi_2O_3 , In_2O_3 and FeO_x can be used as pseudocapacitive anodes. Although lithium-ion batteries are dominantly powering most of today's portable electronics due to the high efficiency and energy density, the high expense and possible unsafety originated from the flammability of organic electrolytes and high reactivity of Li containing materials are two major concerns for our daily life. Instead, aqueous rechargeable batteries (ARBs) with much higher power density and safety have attracted renewed interest as a possible alternative solution.

As an important part of ARBs, aqueous rechargeable lithium batteries (ARLBs) use lithium intercalation compounds as one or two electrodes based on redox reactions and a lithium-containing aqueous solution as the electrolyte [105]. Tang *et al.* [106] successfully prepared LiMn_2O_4 nanotube arrays with an exposed (400) planes by using multiwall carbon nanotubes (MWCNTs) as a sacrificial template. The hybrid material was used as cathode for ARLB, which delivers a high capacity of 110 mA h g^{-1} at 4.5 C and presents very good capacity retention at super-fast second-level charge and discharge rates. Besides this, his group has also devoted effort on anode materials. They coated a polypyrrole layer of 10–12 nm in thickness on a hybrid of V_2O_5 nanowires and MWCNTs [107], which was used as an anode material to construct an ARLB with almost no capacity loss after 500 full cycles.

Our group developed a facile hydrothermal method to fabricate hierarchical nanoarrays-based material for an alkaline battery. We synthesized a hierarchical $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ nanoarray directly grown on conductive substrate, which is desirable for anode material [108]. After that we have designed an alkaline battery by pairing it with hierarchical $\text{Co}_3\text{O}_4\text{@Ni-Co-O}$ nanoarrays electrode as cathode material. The double hierarchical nanoarrays-based aqueous battery (shown in Fig. 10) delivered a high energy density of $\sim 2.08 \text{ mW h cm}^{-2}$, and a power density of $\sim 42.56 \text{ m W cm}^{-2}$ with less than 3 min for one charge-discharge cycle.

CONCLUSIONS AND OUTLOOK

The field of nanoarray materials has flourished in recent years. Due to their unique structure, the nanoarray materials show great promise in EES devices, especially for the transition metal oxides and hydroxides materials. The nanoarray architecture can provide a high surface area, high overall porosity and strong bonding between the active materials and the conductive substrate, which are beneficial to overcome common problems of particle strain and contact loss observed in bulk electrodes, resulting in high specific capacitance, remarkable rate capability and prominent cycling stability. In this review, several synthesis methods and some recent advances in designing and electrochemi-

Figure 10 The schematic drawing of the double hierarchical nanoarrays-based aqueous battery. Reprinted with permission from Ref. [108] (Copyright 2014, Elsevier).

cal applications of nanoarray materials have been summarized. Despite the great progresses, how to further improve the electrochemical performance should be the key point which needs most of the researchers' efforts. Along this direction, several possible future trends are discussed herein.

SCs can provide high power density, superior rate capability, long cycling life. However, the relatively low energy density is mainly restricted by the narrow working potential of aqueous electrolyte. Since the energy density of a SC is proportional to the square of the operating voltage, increasing the operation voltage is regarded as a promising strategy to improve the energy density. Organic electrolytes (up to 2.5–3.0 V) and ionic liquids (up to 4 V) are two ideal options, but they are limited by poor conductivity or high cost. Metal organic framework materials are able to retard the electrolysis of water, thus broadening the voltage window of aqueous electrolytes [109], which may provide a feasible strategy to enhance the energy density in the future.

Another strategy is to pursue high mass-loading of the active materials in a geometric area with high utilization, leading to a high areal capacitance. In our previous studies, hierarchical structures are demonstrated effective to significantly improve the areal capacitance, but the mass-loadings still needs to be increased. Integrating active nanomaterials into the remaining free space in the hierarchical nanoarrays or into the interspace between neighboring arrayed nanostructures should be an effective approach by making full use of voids within the electrode. However, the attendant problems should be taken into consideration carefully. For instance, sufficient porosity of the hybrid structure (hierarchical structure with active nanomaterials) should be maintained for the electrolyte penetration, and the electric connection between the two components

should be optimized.

In industry, the electrode of EES is always made by casting the active materials slurry onto current collectors, while the practical device using nanoarray electrodes is seldom. The synthetic method of nanoarrays is difficult to achieve in industrial level which limits its development. Actually, some excellent nanoarray EES devices have been developed. But the assembly technology and package engineering are also critical to maximize the energy storage performance. In a word, the nanoarray material is in its infancy, and there are still a lot of efforts to be devoted in the future.

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中文摘要 近几年来,人们对于电化学储能设备的需求越来越多,对它的高效性、安全性也越来越重视. 纳米阵列有序结构具有较大的电化学反应比表面积,快速的电子传输和离子扩散,因此可以全面提高电极的比电容、倍率特性以及循环稳定性. 由于具有独特的结构优势,并可以有效地提高电化学储能效果,纳米阵列有序结构成为了电极材料的新选择. 这篇综述总结了近些年来合成金属氧化物或者氢氧化物纳米阵列有序结构材料的策略和方法,以及在水相电解液中超级电容器和电池方面的应用.