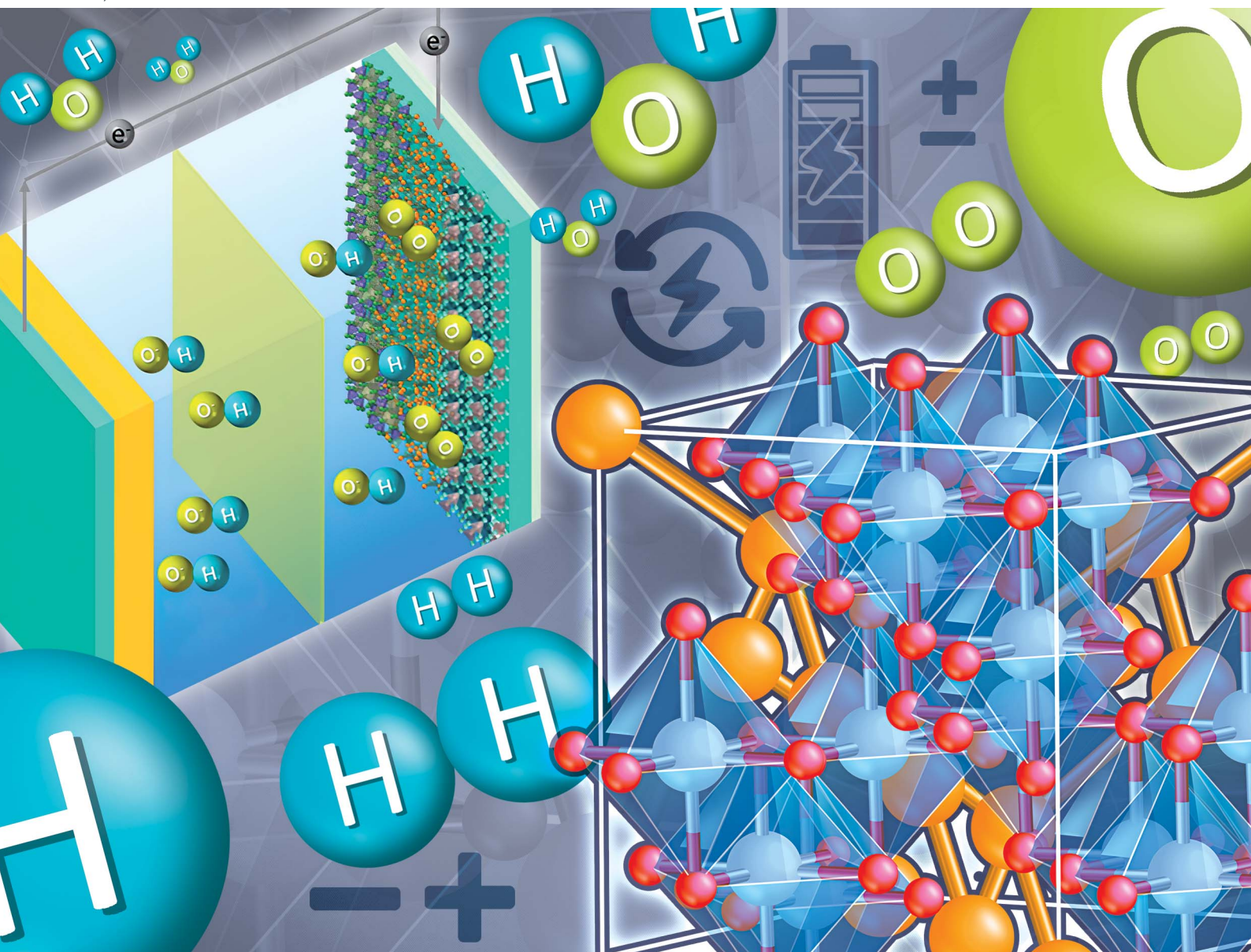


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REVIEW ARTICLE

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Multifunctional spinel MnCo_2O_4 based materials for energy storage and conversion: a review on emerging trends, recent developments and future perspectives



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Multifunctional spinel MnCo_2O_4 based materials for energy storage and conversion: a review on emerging trends, recent developments and future perspectives

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The energy requirement of modern society increases every day. The depletion of the reserves of fossil fuel combined with the deleterious effects of CO_2 in the atmosphere is forcing all the world to search for alternative ways of generation and storing energy. Many scientists around the world are pursuing different forms to produce and store energy. Solar and wind sources are a reality for production of electricity, but are not continuous and require storage devices. The development of batteries and hybrid supercapacitors of high energy and power density is of great importance to complement this requirement of energy storage. Rechargeable metal–air batteries which utilize oxygen electrocatalysis seem to be an ideal choice, once the source of energy is not intermittent as solar and wind energy and is based on oxygen bifunctional electrocatalysis of both oxygen reduction and O_2 evolution reactions. In addition, water splitting allows the conversion and storage of solar/wind energy into chemical energy, generating fuels with high energy content. From this perspective, spinel MnCo_2O_4 -based materials are promising structures for energy storage and conversion of energy. In this review, the use of low cost and abundant multifunctional materials for the development of supercapacitor devices and batteries was summarized. Completely, the design of electrocatalysts for water splitting and their capability to proportionate the tetra-electronic process of the oxygen reduction reaction are reviewed, including the main strategies in the preparation of these materials and considering their key multifunctional role in the way to a more sustainable society.

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1. Introduction

With the increasing demand for environmentally friendly energy sources, alternatives have accelerated research on various renewable energy technologies such as fuel cells, metal-air batteries, and water-splitting devices as alternative energy production and storage systems.¹

However, there are several scientific and technological challenges which require great efforts in the search for a more sustainable society. Among the main challenges, it is easy to identify the scientific race for low-cost and abundant materials for the command of the tetra-protonic and tetra-electronic reaction mechanism of the oxygen evolution reaction (OER),^{2,3} a formidable challenge in the development of H₂ fuel cells. In addition, electrochemical oxygen reduction (ORR) and OER reactions are two key processes that limit the efficiency of important energy conversion devices such as metal-air batteries (MABs) and electrolytic cells.⁴ On the other hand, the quest for much higher power and energy density devices, especially hybrid supercapacitors (HSCs), as alternatives to lithium-ion batteries (LIBs), has been the main objective of several research groups, as they can combine the outstanding power density of supercapacitive materials with the high energy density of battery-type materials into a single device.⁵

In this sense, researchers in materials science have strived to develop advanced and multifunctional materials for modern energy technologies, aiming to overcome the main challenges of energy conversion and storage. In fact, among the several recently studied materials, transition metal oxides (TMOs) have garnered attention due their high electronegativity, rich redox reactions and abundant density of active sites, low cost, environmental friendliness, and excellent electrochemical

performance.⁶ For instance, recently some review articles reported the use of Co₃O₄ and Co₃O₄-containing electrode materials for supercapacitors⁷ and batteries.⁸ In one of these recent



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studies, Hu *et al.*⁹ summarized the proposed strategies for improving specific capacitance, cycling stability, multifunctional capabilities of Co_3O_4 based materials and development prospects of Co_3O_4 -based supercapacitor materials, providing a certain direction for application of Co_3O_4 in supercapacitors in the future. Complementarily, Shi and co-workers⁸ discussed the synthesis and application of pure Co_3O_4 and its composites ($\text{Co}_3\text{O}_4/\text{C}$, $\text{Co}_3\text{O}_4/\text{graphene}$, $\text{Co}_3\text{O}_4/\text{metal oxide}$) in the field of LIBs. On the other hand, in the field of energy conversion, M. R. N. S. Hamdani, R. N. Singh, & P. Chartier (2010)¹⁰ reviewed the performance of Co_3O_4 and Co-based spinel oxides as electrocatalysts for the OER or ORR.

Similar to Co_3O_4 and Co_3O_4 -based materials, manganese-containing TMOs have also been intensively reported for applications in energy technologies,⁶ especially those based on Mn_3O_4 . For example, Zhu *et al.*¹¹ reviewed the electrochemical properties and reaction principles of Mn_3O_4 -based composites with carbon and other metal compounds for supercapacitor electrodes. In addition to the use in supercapacitors, Ubale and colleagues¹² reported the main advances in the deposition, characterization, and applications of nanostructured manganese oxide thin films (NMOTFs) in LIBs, highlighting the structural and morphological studies. On the other hand, Tian and co-workers¹³ reported the emerging applications of a series of MnO_x materials as highly efficient electrocatalysts for the OER, highlighting the reaction mechanisms, superiorities, and challenges of each type of MnO_x for future applications in the highly exciting energy-conversion-related areas.

As already mentioned in the studies cited above, spinel materials with a typical chemical formula of AB_2O_4 have been widely recognized and considered in the energy storage field,¹⁴ and also as electrocatalysts in energy conversion devices. In fact, special attention has been given to spinel materials with bimetallic oxide structure, as they can result in materials with higher electrochemical activity, electrical conductivity, and more abundant redox reactions compared with monometallic oxides of A and B.¹⁵ For example, some reviews reported the recent progress in the use of the NiCo_2O_4 spinel in supercapacitors,¹⁶ batteries¹⁷ and sensors.¹⁸ More recently, Zhao *et al.*¹⁴ summarized the main advances of 2D spinel structured Co-based MCo_2O_4 ($\text{M} = \text{Co}, \text{Ni}, \text{Zn}, \text{Cu}, \text{Fe}, \text{and Mn}$) materials as integrated electrodes for supercapacitor (SC) applications, detailing other different nanomaterials and 2D spinel structured Co-based materials for this application.

To our knowledge, more than five hundred articles report the preparation and/or use of the MnCo_2O_4 spinel for various applications, especially for energy conversion and storage. Thus, this compound has been widely recognized as a promising, versatile, and cost-efficiently bifunctional non-noble-metal electrocatalyst, due to its high redox stability, the complementation and synergy of both transition metals (manganese and cobalt), and efficient variable valence states.^{19–22} As shown earlier, a few of the previous reviews have discussed the applications of Co_3O_4 , Mn_3O_4 and NiCo_2O_4 spinels in energy storage, especially in supercapacitors and LIBs. However, as far as we know, there is no review work



Scheme 1 Illustration of the strategies and applications of MnCo_2O_4 spinels. The atomic structure of the MnCo_2O_4 inverse spinel structure in the center of the scheme was reproduced with permission from ref. 23.

describing the promising results of MnCo_2O_4 in energy technologies. Therefore, in this review article we focus on the recent advances in MnCo_2O_4 -based materials for energy applications and the main strategies used for the design of these materials (Scheme 1), including HSCs, LIBs and MABs, as well as the advancements achieved as electrocatalysts for water-splitting, more specifically for the hydrogen evolution reaction (HER) and OER. The pros and cons of using this spinel in the different devices are critically discussed. Finally, the evolving application of MnCo_2O_4 materials in the ORR is discussed, as well as the perspectives and future directions anticipated.

2. MnCo_2O_4 spinel: a supercapacitive or battery-type material?

The growing and fast demand for clean and sustainable energy storage devices has generated a scientific race for abundant and low-cost materials that can be used in high energy density devices, especially in high power density applications. However, this scientific race has also resulted in a great deal of confusion in the classification of supercapacitive and battery-like materials, especially in the distinction of “pseudocapacitive” and “battery” materials.²⁴ In this sense, several review articles have recently been published in order to alert the scientific community on these misunderstandings.

To clarify the confusion, Chodankar *et al.*²⁴ reported a review article that serves as a guide, providing the meanings and correct performance metrics of different electrode materials and using the electrochemical signatures and quantitative kinetics analysis as a method to distinguish battery-type and pseudocapacitive materials. For instance, electrical double-layer

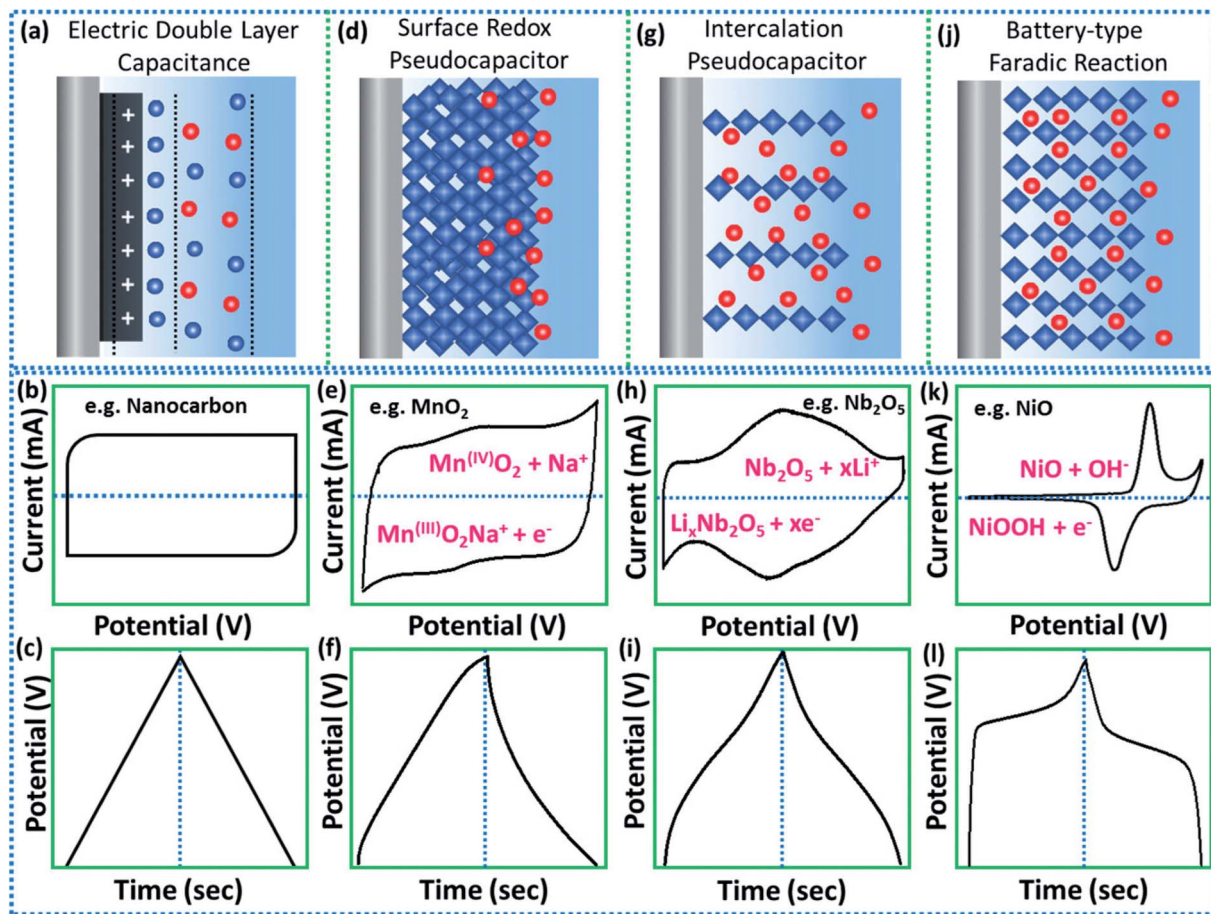


Fig. 1 The schematic illustration of the energy storage mechanisms with their corresponding electrochemical signatures (representative shapes of CV and CD curves): (a–c) electrical double layer capacitance, (d–f) surface redox capacitance, (g–i) intercalation capacitance, and (j–l) faradaic battery-type. Reproduced with permission from ref. 24. Copyright © 2020 Wiley-VCH GmbH.

capacitors (EDLCs) that store energy purely in the double-layer on a high surface area conductor²⁵ show a typical electrochemical signature of a supercapacitive material (Fig. 1a), that is, a rectangular cyclic voltammogram (CV, Fig. 1b) and galvanostatic charge/discharge (GCD) profile in the form of a symmetrical triangle (Fig. 1c). Similarly, pseudocapacitive materials have quasi-rectangular CVs and quasi-triangular GCD curves, however the charge storage mechanisms involve either (a) redox reactions at or near the surface (intrinsic pseudocapacitors); or (b) intercalation-type reactions.²⁴

Surface-redox pseudocapacitors, for example, are well represented by ruthenium (RuO_2) and manganese oxides (MnO_2). In fact, due to their fast proton and electron-conducting properties at the surface of the electrode (Fig. 1d), their electrochemical signatures resemble those of EDLCs, as shown in Fig. 1e and f. In contrast, some layered oxides, such as Nb_2O_5 and MoO_3 , can store energy by faradaic processes through the intercalation of electrolyte ions into the layers (Fig. 1g), especially in a nonaqueous electrolyte system, but without crystallographic phase changes. These materials are of the type “intercalation pseudocapacitors”, but they should not be confused and called redox pseudocapacitors. According to Chodankar *et al.*,²⁴ a way to avoid this confusion is to carefully

analyze the electrochemical features of intercalation pseudocapacitive materials and it was found that (i) they do not undergo phase transformations during intercalation, (ii) their peak potentials do not shift considerably with sweep rate, (iii) their current is linearly proportional to the sweep rate and (iv) their capacity does not vary significantly with charging time.

On the other hand, battery-type electrode materials have an electrochemical signature quite different from supercapacitive materials, since CVs display a couple of redox peaks (Fig. 1k) and plateau GCD profiles (Fig. 1l). This is due to the solid-state diffusion-controlled faradaic reactions characteristic of materials that present phase change of the electrode materials during the electrochemical process (Fig. 1j), such as oxides/hydroxides of Ni, Co, Cu, and Cd that react with hydroxide ions in alkaline media to store a charge.²⁴

Then, is the MnCo_2O_4 spinel a supercapacitive or battery-type material? In the literature it is possible to find some studies that classify MnCo_2O_4 as a supercapacitive material, while others as battery-type. For example, V. Sannasi & K. Subbian²⁶ reported the preparation of high-pseudocapacitance MnCo_2O_4 nanostructures, while S. G. Krishnan, M. H. A. Rahim & R. Jose²⁷ reported the synthesis and characterization of MnCo_2O_4 cuboidal microcrystals as intercalation pseudocapacitors, however, both

studies presented the characteristic electrochemical signature of a battery-like material, such as CVs with a couple of redox peaks and plateau GCD profiles. In addition, peak potentials shifted considerably with sweep rate and capacity varied significantly with charging time. Thus, although many studies classify MnCo_2O_4 as a supercapacitive material, in this review work it was considered as a battery-type material, and in many cases the energy stored in the form of specific charge (C g^{-1}) was recalculated, since the average capacitance (F) was not constant throughout the potential window in the CVs.

In addition, it is also important to clarify that when assembling a battery-type electrode (ex.: MnCo_2O_4) with a supercapacitive-type electrode, a HSC is obtained, matching the advantages from both batteries and supercapacitors, and rendering them promising advanced energy storage devices for commercial applications.²⁸ In fact, experimental and theoretical studies²⁹ (shown below) demonstrated that MnCo_2O_4 has a superior electrical conductivity when compared to Co_3O_4 , also showing greater storage capacity compared to other cobaltite spinels (MCo_2O_4 ; $\text{M} = \text{Ni},^{28} \text{Cu},^{28} \text{Zn}^{30}$ and $\text{Co}^{28,30}$) with good cycling lifespan.²⁹ These characteristics demonstrate the promising possibilities of using these materials in high performance HSCs, as discussed below.

3. MnCo_2O_4 -based materials for energy storage applications

3.1. Supercapacitors

3.1.1. Pristine MnCo_2O_4 . Supercapacitors have received great attention owing to their high energy and power densities. Supercapacitors are highly desirable since this type of device can deliver high power and reasonable energy densities concurrently. Carbonaceous materials, conducting polymers and transition metal oxides have displayed higher energy density compared to other materials.^{31–33} In particular, binary

metal oxides have been considered for supercapacitor electrodes due to their high electrical conductivity relative to single component oxides and advantages of achievable mixed valences.³⁴ MnCo_2O_4 has attracted considerable interest in supercapacitor application since cobalt has a high oxidation potential, whereas manganese can have multiple oxidation states and exhibit higher capacity.³⁵

In addition, it is important for a supercapacitor to have suitable fitting pore size distribution and large specific surface area, aiming to decrease the consumption of electrolyte by regulating the porous structure and morphology of the electrode, which determine the ion diffusion and conductivity, thereby affecting the capacitance of the supercapacitor. MnCo_2O_4 materials with different morphologies, such as spheres,³⁶ granules,³⁷ cuboidal microcrystals,²⁷ nanoneedles,³⁸ nanorods,^{39,40} cubes,^{26,41} nanosheets,^{42–44} nanocages,⁴⁵ tunable porous structures,⁴⁶ hollow spheres,⁴⁷ and network-like porous structures,^{48,49} can be prepared and tested for their usefulness as supercapacitor electrodes. For example, 1D MnCo_2O_4 nanowire arrays showed a specific capacitance of 349.8 F g^{-1} at 1 A g^{-1} and an energy density of 35.4 W h kg^{-1} at a power density of 225 W kg^{-1} .⁵⁰ Similarly, specific capacitances of 1342 F g^{-1} at 1 A g^{-1} and 988 F g^{-1} at 20 A g^{-1} were observed for MnCo_2O_4 nanowires synthesized by Xu *et al.*⁵¹

Liu *et al.*²⁹ reported a MnCo_2O_4 mesoporous nanowire array grown on nickel foam (NF) with a high specific capacitance. From Fig. 2a it is possible to observe that the nanowire has a mesoporous characteristic being formed by MnCo_2O_4 nanoparticles with a size distribution of $\sim 20 \text{ nm}$ (Fig. 2b) and a surface area of $98.5 \text{ m}^2 \text{ g}^{-1}$ (determined from N_2 isotherms). In order to figure out the effect of Mn on the MnCo_2O_4 spinel the projected density of states and electronic band structures were determined and the results are shown in Fig. 2c and d, respectively. Those studies demonstrated that MnCo_2O_4 has a superior electrical conductivity when compared to Co_3O_4 . In fact, MnCo_2O_4 presented a valence bond very near the Fermi



Fig. 2 TEM (a) and HRTEM (b) images of MnCo_2O_4 nanowires, (c and d) projected density of states and electronic band structures of MnCo_2O_4 . (e) GCD curves of MnCo_2O_4 nanowires (black, at 1 A g^{-1}) and (f) cycling performance of MnCo_2O_4 nanowires (black, at 1 A g^{-1}). Reproduced with permission from ref. 29. Copyright © Marketplace™, Royal Society of Chemistry.

level and a low bandgap of 0.35 eV at the G point, in contrast the Co_3O_4 presented a bandgap of 1.72 eV at the same point. Also, the electrochemical behavior of MnCo_2O_4 nanowires was superior to that of Co_3O_4 . A specific capacitance of 2146 F g^{-1} at a current density of 1 A g^{-1} was observed for MnCo_2O_4 nanowires, while for Co_3O_4 the specific capacitance was 948 F g^{-1} ,²⁹ Fig. 2e. In addition, the MnCo_2O_4 nanowires presented an excellent capacitance retention of 92.1% even after 5000 cycles of charge–discharge process, as can be seen in Fig. 2f.

3.1.2. MnCo_2O_4 –metal oxide composite. The recent development of hierarchical nanostructures obtained using metal oxides directly grown on an active material (current collector) showed promising results.⁵² These structures can be modulated in relation to their porosity and contact area between active materials and the electrolyte, providing more active sites in a given unit area without any auxiliary components, resulting in higher electrochemical properties. To link the performance gap between these materials, a variety of core–shell structure electrodes consisting of diverse compounds, such as Co_3O_4 @ MnCo_2O_4 ,^{53,54} MnCo_2O_4 @ MnMoO_4 ,⁵⁵ MnCo_2O_4 @ NiMoO_4 ,^{56,57} and MnCo_2O_4 @ CoMnO_4 have been constructed so far which remarkably improved the electrochemical properties of these materials compared with the individual components. In this way, Shrestha *et al.*⁵⁸ reported a sandwich-type architecture of MnCo_2O_4 @ M-C @ MnO_2 as an electrode material exhibiting an excellent areal/gravimetric capacity of $0.75 \text{ mA h cm}^{-2}/312 \text{ mA h g}^{-1}$ at 3 mA cm^{-2} with a capacity retention of 89.6% after 10 000 cycles. Besides, the hybrid supercapacitor presented an energy density of 68.2 W h kg^{-1} at 749.2 W kg^{-1} power density.

Liu *et al.*⁵⁹ reported the synthesis of a hierarchical MnCo_2O_4 nanowire@ MnO_2 sheet core shell nanostructure showing an energy density of 85.7 W h kg^{-1} at a power density of 800 W kg^{-1} . Zheng and coauthors⁶⁰ also reported a hierarchical MnCo_2O_4 @ MnO_2 core–shell nanowire array exhibiting an energy density of $135.6 \text{ W h kg}^{-1}$ at a power density of 513 W kg^{-1} .

Smarter integrated designs combined with different oxide materials are also reported, such as MnO_2 ,⁶¹ CoO ,⁶² NiWO_4 ,⁶³ ZnO ,⁶⁴ NiO ,⁶⁵ CoCo_2O_4 ,⁶⁶ CuCo_2O_4 ,⁶⁷ NiCo_2O_4 ,⁶⁸ and CoMnO_4 .⁶⁹ These types of structures possess many competitive advantages, including improvement of electrical conductivity, high electron aggregation efficiency, rich approachable electroactive sites, and even excellent synergetic effects or multifunctional properties of the nanostructure components.⁷⁰

3.1.3. MnCo_2O_4 –conducting polymer composites. Conducting polymers can store energy through rapid faradaic charge transfer, since the electrochemical process occurs both on the surface and interface of the electrode material (between the electrode and electrolyte), and due to this, they have been combined with $\text{Mn}_2\text{Co}_2\text{O}_4$ in the form of composites to increase the capacitance.⁷¹ Conducting polymers with high electrical conductivity provide more active sites, which improve the maximum utilization of the MnCo_2O_4 electrode material. The MnCo_2O_4 nanoflakes@polypyrrole (PPy) nanowire electrode displayed a specific capacitance of 2933 F g^{-1} at 20 A g^{-1} .³² Similarly, Wang *et al.*⁷² reported the preparation of

MnCo_2O_4 @PPy nanostructures on graphite foam (GNF), as described in Fig. 3a. The MnCo_2O_4 @PPy/GNF was prepared in different concentrations of PPy, being denoted as MnCo_2O_4 @PPy/GNF-*n*, where *n* was varied from 1 to 6 and the SEM images are shown in Fig. 3b–g. It is possible to observe that PPy grows vertically on MnCo_2O_4 as the concentration of PPy increases, thus forming interconnected network nanosheets. The MnCo_2O_4 @PPy/GNF-5 exhibited a specific capacitance of 2364 F g^{-1} and a rate capability of 55.2% from 1 to 50 A g^{-1} .

Furthermore, a HSC was built with MnCo_2O_4 @PPy/GNF-5 and activated microwave exfoliated graphite oxide (a-MEGO) as positive and negative electrodes, respectively. The HSC showed an energy density of 25.7 W h kg^{-1} and a power density of 16.1 kW kg^{-1} , besides a capacitance retention of 85.5% after incredible 10 000 cycles (Fig. 3h). Hu *et al.*⁷³ also reported a composite based on PPy decorated by MnCo_2O_4 urchins showing an energy density of $0.785 \text{ mW h cm}^{-1}$ at a power density of 7.49 W cm^{-1} as the positive electrode for supercapacitors.

3.1.4. MnCo_2O_4 –carbon based composites. Materials based on carbon structures have a large specific surface area, good electrical conductivity and strong mechanical strength, thus becoming leading materials for the electrodes applied for supercapacitors. However, the specific capacitance of carbon is much lower than that of transition metal oxides, which limits their practical applications to a certain degree. Fortunately, carbon modifications can improve the electrical conductivity of MnCo_2O_4 -based electrode materials.^{74,75} Moreover, the combined effects of MnCo_2O_4 structure with different materials of conducting carbons, such as graphene,^{31,33,76,77} activated carbon,^{78,79} carbon nanofibers,⁸⁰ carbon aerogels,⁸¹ reduced graphene oxide (rGO),^{82,83} carbon nanotubes (CNTs), and graphene quantum dots,⁸⁴ are very promising to improve the overall performance of the system. In this way, Saren *et al.*⁸⁵ reported the preparation of flower-like hybrid spinel MnCo_2O_4 @graphene nanosheets and MnCo_2O_4 @CNT nanocomposites by a hydrothermal method for supercapacitor application. A specific capacitance of 923.97 F g^{-1} , an energy density of $82.13 \text{ W h kg}^{-1}$ and a power density of 399.74 W kg^{-1} at a current density of 1 A g^{-1} were observed for MnCo_2O_4 @graphene nanosheets, while a specific capacitance of 579.71 F g^{-1} was achieved for MnCo_2O_4 @CNT.

Wu and coworkers⁷⁷ developed a new bifunctional composite based on MnCo_2O_4 /nanographene (B-*n*- MnCo_2O_4) prepared on a macroporous electrically conductive network (MECN) as an electrode material for supercapacitors and sodium ion batteries. The 3D structure of nanographene coating MECN and B-*n*- MnCo_2O_4 @MECN can be seen in Fig. 3i–l. Fig. 3i and k show nanographene layers with a lateral size of 50–200 nm and when the B-*n*- MnCo_2O_4 was incorporated onto the MECN (Fig. 3j and l) the 3D nanostructure displayed a uniform diameter of $\sim 50 \text{ nm}$. This 3D interconnected morphology seems to be very interesting since it can improve the electronic conductivity, in addition to facilitating electrochemical reactions, because of its large surface area. The B-*n*- MnCo_2O_4 @MECN presented a high specific capacitance of 7.02 F cm^{-2} (2341 F g^{-1}) at 3 mA cm^{-2} . The specific capacitance of B-*n*-

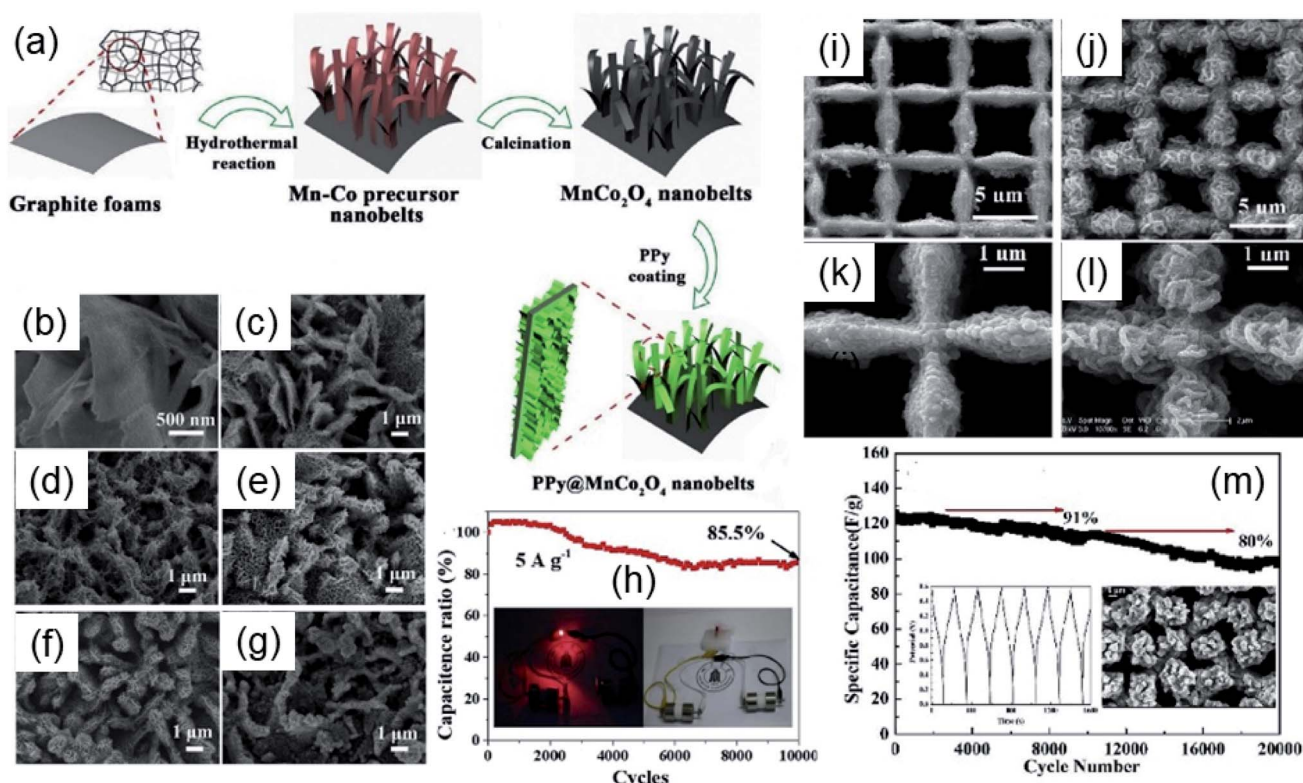


Fig. 3 Scheme of the synthesis process of PPy@MnCo₂O₄/GNF (a), SEM images of the PPy@MnCo₂O₄/GNF-*n* (*n* = 1–6) (b–g) and cycling stability performance of the hybrid supercapacitor PPy@MnCo₂O₄/GNF-5//a-MEGO (h). Reproduced with permission from ref. 72. Copyright © 2018 Elsevier B.V. All rights reserved. SEM images of nanographene@MECN at low (i) and high magnification (k) and B-*n*-MnCo₂O₄@MECN at low (j) and high magnification (l). Stability electrochemical performance of the hybrid supercapacitor B-*n*-MnCo₂O₄@MECN//AC@Ni foam (m). Reproduced with permission from ref. 77. Copyright © 2020 Elsevier B.V. All rights reserved.

MnCo₂O₄@MECN is much larger than that of Mn₃O₄/nanographene@MECN (2.7 F cm⁻²) and Co₃O₄/nanographene@MECN (2.2 F cm⁻²) at the same current density, which highlights the presence of MnCo₂O₄ in the composite.

Also, a HSC was built with B-*n*-MnCo₂O₄@MECN and AC@Ni foam as positive and negative electrodes, respectively. The device provided an outstanding long lifetime and stability as well. Even after incredible 20 000 charge–discharge cycles the device showed a capacitance retention of 80%, as can be seen in Fig. 3m. The long lifetime can be attributed to good adhesion between all the components and good electrical contact between B-*n*-MnCo₂O₄ and MECN as the current collector.

3.1.5. Other MnCo₂O₄-based composite materials.

MnCo₂O₄@CoS,⁸⁶ MnCo₂O₄/Ni,^{87,88} MnCo₂O₄@nitrogen-doped carbon,⁸⁹ MnCo₂O₄/Ni/Cu,⁹⁰ MnCo₂O₄@Co(OH)₂,⁹¹ and MnCo₂O₄@Ni(OH)₂ belts⁹² are also introduced as positive electrodes for supercapacitor applications, which delivered capacitances comparable with those of the previously discussed composites. For example, Lv *et al.*⁹³ reported a novel self-supported MnCo₂O₄@Ni₃S₂ core–shell heterostructure, showing a specific capacitance of 2807 F g⁻¹ at 3 A g⁻¹. The same research group⁹⁴ also described a hierarchical MnCo₂O₄/NiMn composite deposited on Ni foam. The layer-by-layer architecture combined with the synergistic effect of both components of the composite provided a specific capacitance of

3063 F g⁻¹ at 3 A g⁻¹ and a cycle stability of 94.7% at 20 A g⁻¹ over 5000 cycles.

Most of the materials previously-mentioned were deposited on Ni foam as the conductive substrate,^{27,57,60,65} which did not require the addition of polymer binders, and promoted rapid electron transport between the active material and current collector, thereby resulting in a substantially efficient substrate, due to the high electrical conductivity (1.43 × 10⁷ Ω⁻¹) and thermal conductivity (90.7 W mK⁻¹) of Ni.⁹⁰ Nevertheless, other conductive substrates and current collectors have also been employed, such as carbon aerogels,⁸¹ graphite foam,⁷² indium-doped tin oxide,⁴⁴ activated carbon,⁷⁸ microporous electrically conductive networks,⁷⁷ graphite paper,^{59,67,95} carbon fiber paper⁹⁶ and copper foil.³⁵ Table 1 presents the performance of different supercapacitor materials coupled with different types of electrodes based on MnCo₂O₄.

3.2. Batteries

3.2.1. Lithium-ion batteries.

Rechargeable Li-ion batteries (LIBs) were shown as the most efficient energy storage devices, since the small size of lithium ions makes their diffusion more favorable in a variety of structures.¹⁰³ Spinel binary transition-metal oxide materials, such as MnCo₂O₄, have been widely investigated as anode electrodes for LIBs, due to their lower cost and better electronic conductivity than single-metal oxides.^{104,105}

Table 1 Performances of some reported MnCo₂O₄-based supercapacitors^a

Type	Material	Specific capacitance (F g ⁻¹)	Potential window (V vs.)	Retention (%) rate capability (A g ⁻¹)	Cycling stability	Highest energy density (W h kg ⁻¹)	Highest power density: (kW kg ⁻¹)	Negative electrode material	Ref.
Pristine	Flake-like MnCo ₂ O ₄	1487 F g ⁻¹ at 594.8 C g ⁻¹ 1 A g ⁻¹	0.0–0.4 V (vs. SCE)	—	93.3% (2000 cycles)	—	—	—	35
	MnCo ₂ O ₄	405 F g ⁻¹ at 1 mA cm ⁻²	0–0.4 V (vs. SCE)	67.9%, (5–40 mA cm ⁻²)	95.1% (1000 cycles)	—	—	—	37
	MnCo ₂ O ₄ nanorods	845 F g ⁻¹ at 422.5 C g ⁻¹ 1 A g ⁻¹	0.0–0.5 V (vs. Hg/HgO)	51.6%, (1–20 A g ⁻¹)	90.2% (2000 cycles)	53.7	8	rGO/NF	39
	MnCo ₂ O ₄ nanorods	718.75 F g ⁻¹ at 287.5 C g ⁻¹ 0.5 A g ⁻¹	0.0–0.4 V (vs. Ag/AgCl)	—	100% (1000 cycles)	—	—	—	40
	MnCo ₂ O ₄ hollow spheres	0.8 F cm ⁻² at 2 0.32 C cm ⁻² mA cm ⁻²	0.0–0.4 V (vs. SCE)	—	99% (2000 cycles)	0.052 mW h cm ⁻³	320 mW cm ⁻³	AC/CFs	47
	Porous sphere MnCo ₂ O ₄	1044 F g ⁻¹ at 574.2 C g ⁻¹ 0.5 A g ⁻¹	0.0–0.55 V (vs. Hg/HgO)	68.9%, (1–20 A g ⁻¹)	133.3% (10 000 cycles)	42.27	0.4	Starch-derived carbon foam	36
	Network-like porous MnCo ₂ O ₄	647.42 F g ⁻¹ at 323.71 C g ⁻¹ 1 A g ⁻¹	0.1–0.6 V (vs. Hg/HgO)	70.67%, (1–10 A g ⁻¹)	93.68% (3000 cycles)	—	—	—	48
	MnCo ₂ O ₄ nanowires	2146 F g ⁻¹ at 858.4 C g ⁻¹ 1 A g ⁻¹	0.0–0.4 V (vs. SCE)	—	92.1% (5000 cycles)	29.3	8	AC	29
	MnCo ₂ O ₄ nanowires	405 F g ⁻¹ at 202.5 C g ⁻¹ 1 A g ⁻¹	0.0–0.5 V (vs. Hg/HgO)	51.4%, (1–10 A g ⁻¹)	91% (4000 cycles)	—	—	—	97
	MnCo ₂ O ₄ nanowires	1342 F g ⁻¹ at 738.1 C g ⁻¹ 1 A g ⁻¹	0.0–0.55 V (vs. Hg/HgO)	73.6%, (1–20 A g ⁻¹)	—	—	—	—	51
	MnCo ₂ O ₄ nanowires	349.8 F g ⁻¹ at 157.4 C g ⁻¹ 1 mV s ⁻¹	0.0–0.45 V (vs. Ag/AgCl)	94%, (1–20 A g ⁻¹)	94% (4000 cycles)	33.3	4.5	—	50
	MnCo ₂ O ₄ nanoparticles	1068.5 F g ⁻¹ at 427.2 C g ⁻¹ 1 A g ⁻¹	0.0–0.4 V (vs. SCE)	50%, (1–8 A g ⁻¹)	90% (2000 cycles)	—	—	—	26
	Chestnut-like MnCo ₂ O ₄ nanoneedles	1535 F g ⁻¹ at 921 C g ⁻¹ 1 A g ⁻¹	0.0–0.6 V (vs. SCE)	61.8%, (1–10 A g ⁻¹)	94.3% (12 000 cycles)	~60.4	~0.375	Graphene/NF	38
	MnCo ₂ O ₄ nanosheets	2000 F g ⁻¹ at 1000 C g ⁻¹ 0.5 A g ⁻¹	0.0–0.5 V (vs. Hg/HgO)	57.5%, (0.5–20 A g ⁻¹)	92.3% (5000 cycles)	73.95	15	rGO	42
	Nanocage MnCo ₂ O ₄	1763 F g ⁻¹ at 969.65 C g ⁻¹ 1 A g ⁻¹	0.0–0.55 V (vs. Hg/HgO)	—	95% (4500 cycles)	54.15	0.324	Nanocage MnCo ₂ O ₄	45
	Flower-like MnCo ₂ O ₄	249.3 F g ⁻¹ at 174.5 C g ⁻¹ 0.5 A g ⁻¹	–0.3–0.4 V (vs. Hg/HgO)	78.8%, (0.5–5 A g ⁻¹)	93.6% (2000 cycles)	—	—	—	98
	Flower-like MnCo ₂ O ₄	571 F g ⁻¹ at 285.5 C g ⁻¹ 0.5 A g ⁻¹	–0.1–0.4 V (vs. Hg/HgO)	87.7%, (0.5–5 A g ⁻¹)	96.1% (2000 cycles)	—	—	—	99
	MnCo ₂ O ₄ cubes	480.5 F g ⁻¹ at 264.3 C g ⁻¹ 1 A g ⁻¹	0.0–0.55 V (vs. Hg/HgO)	75.7%, (1–25 A g ⁻¹)	96.6% (3000 cycles)	—	—	—	41
	MnCo ₂ O ₄ cuboidal microcrystals	600 F g ⁻¹ at 300 C g ⁻¹ 0.5 A g ⁻¹	0.0–0.5 V (vs. Ag/AgCl)	55.7%, (0.5–5 A g ⁻¹)	132% (3000 cycles)	—	—	—	27
	MnCo ₂ O ₄	270 F g ⁻¹ at 10 mV s ⁻¹	–1.2–1.5 V (vs. Ag/AgCl)	—	92.4% (1000 cycles)	14.85	0.495	—	49

Table 1 (Contd.)

Type	Material	Specific capacitance (F g ⁻¹)	Specific capacity (C g ⁻¹)	Potential window (V vs.)	Retention (%), rate capability (A g ⁻¹)	Cycling stability	Highest energy density (W h kg ⁻¹)	Highest power density: (kW kg ⁻¹)	Negative electrode material	Ref.
	Porous MnCo ₂ O ₄	151 F g ⁻¹ at 5 mV s ⁻¹	—	0–0.5 V (vs. SCE)	83.6%, (0.1–5 A g ⁻¹)	—	—	—	—	95
	MnCo ₂ O ₄ nanosheets	—	282 C g ⁻¹ at 1 A g ⁻¹	0–0.55 V (vs. SCE)	25.2%, (1–10 A g ⁻¹)	84% (1500 cycles)	2.55	37.57	FeMn ₂ O ₄	43
	MnCo ₂ O ₄ nanorods	187.0 F g ⁻¹ at 0.25 A g ⁻¹	51.9 C g ⁻¹	0.0–0.4 V (vs. Ag/AgCl)	8%, (0.25–30 A g ⁻¹)	90% (2000 cycles)	12.77	2.520	AC	100
	MnCo ₂ O ₄ nanosheets	250 F g ⁻¹ at 0.25 A g ⁻¹	100 C g ⁻¹	0.0–0.4 V (vs. Ag/AgCl)	10.8%, (0.25–10 A g ⁻¹)	95% (1000 cycles)	10.04	5.2	—	44
MnCo ₂ O ₄ -metal oxide	Co ₃ O ₄ @MnCo ₂ O ₄	736.5 F g ⁻¹ at 1 mA cm ⁻²	—	0–0.5 V (vs. SCE)	—	79.95% (3000 cycles)	—	—	—	53
	MnCo ₂ O ₄ @Co ₃ O ₄	—	1440 C cm ⁻² at 1 mA cm ⁻²	0.0–0.45 V (vs. SCE)	—	101.23% (8000 cycles)	31	0.208	AC	54
	MnCo ₂ O ₄ @CoMnO ₄	2115.38 F g ⁻¹ at 1.1 A g ⁻¹	1100 C g ⁻¹	0.0–0.52 V (vs. Hg/HgO)	47.4%, (1.1–6.6 A g ⁻¹)	119% (5000 cycles)	37.5	0.527	AC	69
	MnCo ₂ O ₄ @CoCo ₂ O ₄	614 F g ⁻¹ at 1 A g ⁻¹	276.3 C g ⁻¹	0.0–0.45 V (vs. SCE)	76.9%, (1–10 A g ⁻¹)	77.5% (5000 cycles)	—	—	—	66
	MnCo ₂ O ₄ @NiMoO ₄	1718 F g ⁻¹ at 1 A g ⁻¹	859 C g ⁻¹	0.0–0.5 V (vs. Hg/HgO)	69.8%, (1–8 A g ⁻¹)	84% (6000 cycles)	42.3	0.797	AC	56
	CuCo ₂ O ₄ /MnCo ₂ O ₄	1434 F g ⁻¹ at 0.5 A g ⁻¹	860.4 C g ⁻¹	0.0–0.6 V (vs. SCE)	56.6%, (0.5–15 A g ⁻¹)	81.4% (5000 cycles)	42.1	0.4	Graphene/NF	67
	MnCo ₂ O ₄ @NiMoO ₄	1244 F g ⁻¹ at 1 A g ⁻¹	746.4 C g ⁻¹	0.0–0.6 V (vs. SCE)	91%, (1–10 A g ⁻¹)	81% (2500 cycles)	42	0.8	AC	57
	NiCo ₂ O ₄ -MnCo ₂ O ₄	1152 F g ⁻¹ at 1 A g ⁻¹	576 C g ⁻¹	0.0–0.5 V (vs. Ag/AgCl)	72.2%, (1–10 A g ⁻¹)	95.4% (3000 cycles)	40	0.2	—	68
	MnO ₂ /MnCo ₂ O ₄	497 F g ⁻¹ at 0.5 A g ⁻¹	248.5 C g ⁻¹	0.0–0.5 V (vs. Hg/HgO)	62.8%, (0.5–10 A g ⁻¹)	60% (5000 cycles)	—	—	—	61
	MnCo ₂ O ₄ @NiO	508.3 F g ⁻¹ at 2 A g ⁻¹	279.6 C g ⁻¹	0.0–0.55 V (vs. SCE)	67.7%, (0.5–6 A g ⁻¹)	89.7% (2000 cycles)	—	—	—	65
	MnCo ₂ O ₄ @NiWO ₄	5.09 F cm ⁻² at 1 mA cm ⁻²	2.54 C cm ⁻²	0.0–0.5 V (vs. Hg/HgO)	26.1%, (1–20 mA)	96% (5000 cycles)	0.23 mW h cm ⁻²	2.66 mW cm ⁻²	AC	63
	CoO/MnO ₂ /MnCo ₂ O ₄ composite nanowires	1650 F g ⁻¹ at 1 A g ⁻¹	660 C g ⁻¹	0.0–0.4 V (vs. Ag/AgCl)	60.0%, (1–15 A g ⁻¹)	—	90	10	CoO/MnO ₂ /MnCo ₂ O ₄ composite nanowires	62
	rMnCo ₂ O ₄ @rMnO ₂	3.39 F cm ⁻² at 3 mA cm ⁻²	0.4 mA h cm ⁻²	0.0–0.4 V (vs. SCE)	48.9%, (3–60 mA)	92.5% (3000 cycles)	32.4	4.524	AC	101
	MnCo ₂ O ₄ @MnO ₂ core-shell arrays	2262 F g ⁻¹ at 1 A g ⁻¹	904.8 C g ⁻¹	0.0–0.4 V (vs. SCE)	48.8%, (1–20 A g ⁻¹)	87.1% (5000 cycles)	34.7	24	Graphene/NF	59
	ZnO@MnCo ₂ O ₄	631.2 F g ⁻¹ at 1 A g ⁻¹	504.9 C g ⁻¹	–0.2–0.6 V (vs. SCE)	31.7%, (1–10 A g ⁻¹)	92.3% (1000 cycles)	56.10	0.4	—	64
	NiCo ₂ O ₄ -MnCo ₂ O ₄ rose-like composite	1100 F g ⁻¹ at 1 A g ⁻¹	440 C g ⁻¹	0.0–0.4 V (vs. SCE)	69.1%, (1–10 A g ⁻¹)	—	—	—	—	102

Table 1 (Contd.)

Type	Material	Specific capacitance (F g ⁻¹)	Potential window (V vs.)	Retention (%), rate capability (A g ⁻¹)	Cycling stability	Highest energy density (W h kg ⁻¹)	Highest power density: (kW kg ⁻¹)	Negative electrode material	Ref.
MnCo ₂ O ₄ -conducting polymer	MnCo ₂ O ₄ @MnMoO ₄ core-shell	—	0.0–0.4 V (vs. SCE)	71%, (3–30 A g ⁻¹)	95% (5000 cycles)	49.4	0.815	AC	55
	MnCo ₂ O ₄ @PPy/GNF	2933 F g ⁻¹ at 2 A g ⁻¹	0.0–0.5 V (vs. Ag/AgCl)	55.3%, (2–20 A g ⁻¹)	86.7% (5000 cycles)	78.2	1.121	AC	32
	MnCo ₂ O ₄ @PPy	—	0.0–0.5 V (vs. Hg/HgO)	84.5%, (1–10 mA cm ⁻²)	88% (2000 cycles)	0.785 mW h cm ⁻³	7.49 mW cm ⁻³	AC	73
MnCo ₂ O ₄ -carbon based composites	Polypyrrole@MnCo ₂ O ₄ /graphite foam	2364 F g ⁻¹ at 1 A g ⁻¹	–0.1–0.4 V (vs. Ag/AgCl)	55.2%, (1 to 50 A g ⁻¹)	85.3% (1000 cycles)	25.7	16.1	a-MEGO	72
	MnCo ₂ O ₄ /graphene	503 F g ⁻¹ at 1 A g ⁻¹	0.0–0.4 V (vs. SCE)	65.5%, (1–20 A g ⁻¹)	97.4% (5000 cycles)	—	—	—	76
	Flower-like MnCo ₂ O ₄ /rGO	923.97 F g ⁻¹ at 1 A g ⁻¹	0.0–0.8 V (vs. Ag/AgCl)	—	111% (5000 cycles)	82.13	0.399	Carbon black	85
Other MnCo ₂ O ₄ -based composite materials	MnCo ₂ O ₄ @nitrogen doped graphene@C@MnCo ₂ O ₄	1170 F g ⁻¹ at 1 A g ⁻¹	0.0–0.5 V (vs. Ag/AgCl)	69.9%, (1–20 A g ⁻¹)	87.6% (5000 cycles)	48.5	~0.808	Nitrogen doped graphene hydrogel	33
	MnCo ₂ O ₄ @activated carbon	728.4 F g ⁻¹ at 1 A g ⁻¹	0.0–0.5 V (vs. Ag/AgCl)	71.3%, (1–10 A g ⁻¹)	—	25.5	0.856	—	79
	MnCo ₂ O ₄ @activated carbon	—	–1.0–0.4 V (vs. SCE)	—	66.95% (5000 cycles)	—	—	—	78
Other MnCo ₂ O ₄ -based composite materials	MnCo ₂ O ₄ graphene quantum dots	1625 F g ⁻¹ at 1 A g ⁻¹	0.0–0.5 V (vs. Hg/HgO)	80%, (0.5–10 A g ⁻¹)	80% (5000 cycles)	46	0.066	rGO	84
	B-n-MnCo ₂ O ₄ @MECN	7.02 F cm ⁻² at 3 mA cm ⁻²	–0.1–0.45 V (vs. Hg/HgO)	31%, (3–20 mA cm ⁻²)	98% (5000 cycles)	50.5	6.4	AC/NF	77
	MnCo ₂ O ₄ @Co(OH) ₂	1185 C g ⁻¹ at 1 A g ⁻¹	0.0–0.5 V (vs. SCE)	78%, (1–20 A g ⁻¹)	96% (5000 cycles)	67.2	0.8	N-CNTs@rGO	91
	MnCo ₂ O ₄ @Ni(OH) ₂	2154 F g ⁻¹ at 5 A g ⁻¹	0.0–0.45 V (vs. SCE)	32.6%, (5–20 A g ⁻¹)	90% (2500 cycles)	48	14.9	MnCo ₂ O ₄ @Ni(OH) ₂	92
	MnCo ₂ O ₄ @Ni ₃ S ₂ core-shell heterostructures	2807 F g ⁻¹ at 3 A g ⁻¹	0.0–0.4 V (vs. SCE)	69.0%, (3–30 A g ⁻¹)	92% (5000 cycles)	—	—	—	93
	MnCo ₂ O ₄ @NiMn	3063 F g ⁻¹ at 3 A g ⁻¹	0.0–0.45 V (vs. SCE)	75.6%, (3–30 A g ⁻¹)	94.7% (5000 cycles)	51.9	0.8	AC	94
	Dual-MnCo ₂ O ₄ /Ni	2265 F g ⁻¹ at 1.7 A g ⁻¹	0.0–0.45 V (vs. Ag/AgCl)	70%, (2–10 mA cm ⁻²)	85% (2000 cycles)	—	—	—	88
	MnCo ₂ O ₄ @CoS	1607.4 F g ⁻¹ at 0.8 A g ⁻¹	0.0–0.45 V (vs. SCE)	—	91.5% (5000 cycles)	55.1	0.477	AC	86

^a AC = activated carbon; a-MEGO = activated microwave exfoliated graphite oxide; CFs = carbon fibres; rGO = reduced graphene oxide; NF = nickel foam; N-CNTs = N-doped carbon nanotubes; PPy = polypyrrole; rMnCo₂O₄@rMnO₂ = reduced core-shell structured MnCo₂O₄@MnO₂. * By cyclic voltammetry.

A large variety of nanoscale building blocks of MnCo_2O_4 have been widely investigated, especially due to their good electrochemical performance.¹⁰⁶

In order to improve the electrochemical performance of MnCo_2O_4 structures as anodic materials in LIBs, morphological modifications and synthesis methods have been the focus of investigations.^{107–113} One of these strategies has been focused on the preparation of porous MnCo_2O_4 materials^{114,115} and on the development of diverse substrates as current collectors (carbon cloth,^{116–118} Ni foam¹¹³ and copper foil^{115,119}) with robust adhesion to obtain a binder-free anode material. Li *et al.*¹²⁰ first developed a two-step method to prepare uniform hollow MnCo_2O_4 submicrospheres with multilevel interiors (mesoporous, hollow, yolk-shell, shell-in-shell, and yolk-in-double-shell spheres). The yolk-shell morphology (Fig. 4a) showed the best performance among these multilevel interior structures, with an initial discharge capacity of 1425 mA h g^{-1} at a current density of 400 mA g^{-1} (Fig. 4b). Huang *et al.*¹²¹ also fabricated spherical yolk-shell MnCo_2O_4 powders (Fig. 4c) by a hydrothermal method followed by a thermal treatment, with an initial discharge capacity of 1445 mA h g^{-1} at 0.2 A g^{-1} and capacity retention of $\sim 860.0 \text{ mA h g}^{-1}$ after 40 cycles at 0.2 A g^{-1} (Fig. 4d). The literature reports the preparation of different MnCo_2O_4 porous based structures for anode electrodes, such as spheres,^{122,123} yolk-shell microspheres¹²⁴ (Fig. 4e and f), microflowers,¹²⁵ hydrangea-like structures,¹²⁶ and dumbbell-shaped structures.¹²⁷

Fu *et al.*¹⁰⁶ reported the preparation of microspheres of MnCo_2O_4 by a calcination-free method; in this work, two kinds of MnCo_2O_4 crystals with different exposed facets of $(\bar{1}10)$ and $(1\bar{1}2)$ were synthesized, presenting two different morphologies, particle-assembled and sheet-assembled microspheres, respectively. The anode was evaluated, and the microspheres delivered a capacity of 722 mA h g^{-1} after 25 cycles at a current density of 200 mA g^{-1} , and capacities up to 553 and 320 mA h g^{-1} after 200 cycles at a current density of 400 and 900 mA g^{-1} , respectively.

Huang and colleagues¹²⁸ proposed a novel core-shell ellipsoidal MnCo_2O_4 powder with a desired micro-/nano-structure and unique concentration gradient. The battery tests demonstrated excellent values of initial discharge capacities ($1433.3 \text{ mA h g}^{-1}$ at 0.1 A g^{-1} and $1248.4 \text{ mA h g}^{-1}$ at 0.4 A g^{-1}), capacity retention ($\sim 900.0 \text{ mA h g}^{-1}$ after 60 cycles at 0.1 A g^{-1}) and rate performance ($\sim 620.0 \text{ mA h g}^{-1}$ after 50 cycles at 0.4 A g^{-1}).

Developing composites of MnCo_2O_4 with other materials is an important strategy to improve the performance of LIBs.^{129,130} A 3D sandwich-shape graphene based nanocomposite intercalated with double-shelled hollow MnCo_2O_4 spheres as an anode material for LIBs has been synthesized, showing a rate capability of 538 mA h g^{-1} at a current density of 1000 mA g^{-1} and outstanding cycle performance, with a capability of 703 mA h g^{-1} after 100 cycles at 200 mA g^{-1} .¹³¹ The literature also reports the synthesis of MnCo_2O_4 containing nickel,^{132,133} Co_3O_4 ,¹¹⁹ CoO ,¹¹⁸ MnO_2 ,¹³⁴ TiO_2 ,¹³⁵ and NiCo_2O_4 .¹⁰² Huang and coauthors¹³⁶ designed a MnCo_2O_4 @N-doped carbon@ MnO_2 three layered core shell octahedron as an anode material for Li-ion storage, which displayed a discharge capacity of

894 mA h g^{-1} at a current density of 500 mA g^{-1} after 120 cycles. Even at a high current density of 1000 mA g^{-1} , the discharge capacity remained at 839 mA h g^{-1} after 600 cycles.

Some conductive substrates have also served as current collectors to further improve the electrochemical performance of electrode materials, including carbon materials and conductive polymers, which have been mixed with MnCo_2O_4 structures,^{137,138} such as graphene,¹³⁹ CNTs,¹⁴⁰ carbon cloth^{116,117} and PPy.¹⁴¹ Hence, the construction of composites with the combination of two or more different materials has been proved as a promising strategy to boost the electrochemical performance of MnCo_2O_4 . Due to the electronic conductivity and the specific surface area, rGO has been considered for the formation of composites with MnCo_2O_4 . Fan *et al.*¹⁴² reported the synthesis of MnCo_2O_4 /rGO composites with an initial discharge capacity of 1657 mA h g^{-1} at a current density of 0.1 A g^{-1} , and a reversible capacity of 791 mA h g^{-1} at 0.2 A g^{-1} for 100 cycles. A MnCo_2O_4 @PANi-rGO composite was also synthesized by Huang *et al.*,¹⁴³ with a discharge capacity of 745 mA h g^{-1} and a coulombic efficiency of 100% after 1050 cycles at a current density of 500 mA g^{-1} .

3.2.2. Sodium ion batteries. Operating with similar chemistry to Li-ion electrodes, sodium-ion batteries (SIBs) are under intense investigation to overtake LIBs with the advantages of low-cost and safety. Wu and coworkers¹⁴⁴ reported mesoporous Ni-doped MnCo_2O_4 hollow nanotubes (MCNO-HNTs) as an anode in SIBs, with a remarkable capacity retention of 81% at 1 A g^{-1} even after 11 000 cycles. Flower-like MnCo_2O_4 synthesized by a co-precipitation method exhibited a discharge capacity of 244 mA h g^{-1} after 40 cycles at 50 mA h g^{-1} , which corresponds to 77.1% compared with the second discharge capacity cycle.¹⁴⁵ Table 2 summarizes the performance of different cells of metal ion batteries coupled with different types of electrodes based on MnCo_2O_4 .

3.2.3. Li-O₂ batteries. Lithium-oxygen batteries have a specific potential energy density of approximately 1700 W h kg^{-1} , which is 5-fold higher than that of conventional current LIBs. This type of device has also significant advantage in their gravimetric energy densities.¹⁴⁹ Transition metal oxides, such as MnCo_2O_4 , have been investigated as cathodes for Li-O₂ batteries,^{150,151} especially due to their low-cost catalyst, good stability, high activity, and simple preparation.¹⁵² Wu *et al.*¹⁵³ reported hierarchical porous 3D MnCo_2O_4 nanowire bundles as a cathode for Li-O₂ cell application (Fig. 5a), which exhibited specific capacities of 500 and 1000 mA h g^{-1} over 300 and 144 cycles, respectively, and a discharge capacity of $12\,919 \text{ mA h g}^{-1}$ at 0.1 mA cm^{-2} . More importantly, after two months of cycling, the microstructure of the cathode was maintained and a recyclability of over 200 cycles was achieved. Other structures with high electrochemical performance can be obtained, such as nanotubes¹⁵⁴ (Fig. 5b) and spheres^{155,156} (Fig. 5c). Composites are also explored to maximize the electrochemical performance of Li-O₂ batteries, particularly highlighting materials containing porous carbon,¹⁵⁷ Ti_4O_7 ¹⁵⁸ and MoO_2/Ni ¹⁵⁹.

Large surface areas can provide a promising electrocatalytic activity for the ORR and OER in Li-O₂ batteries. In this way, to enhance the charge transfer rate, composites between MnCo_2O_4

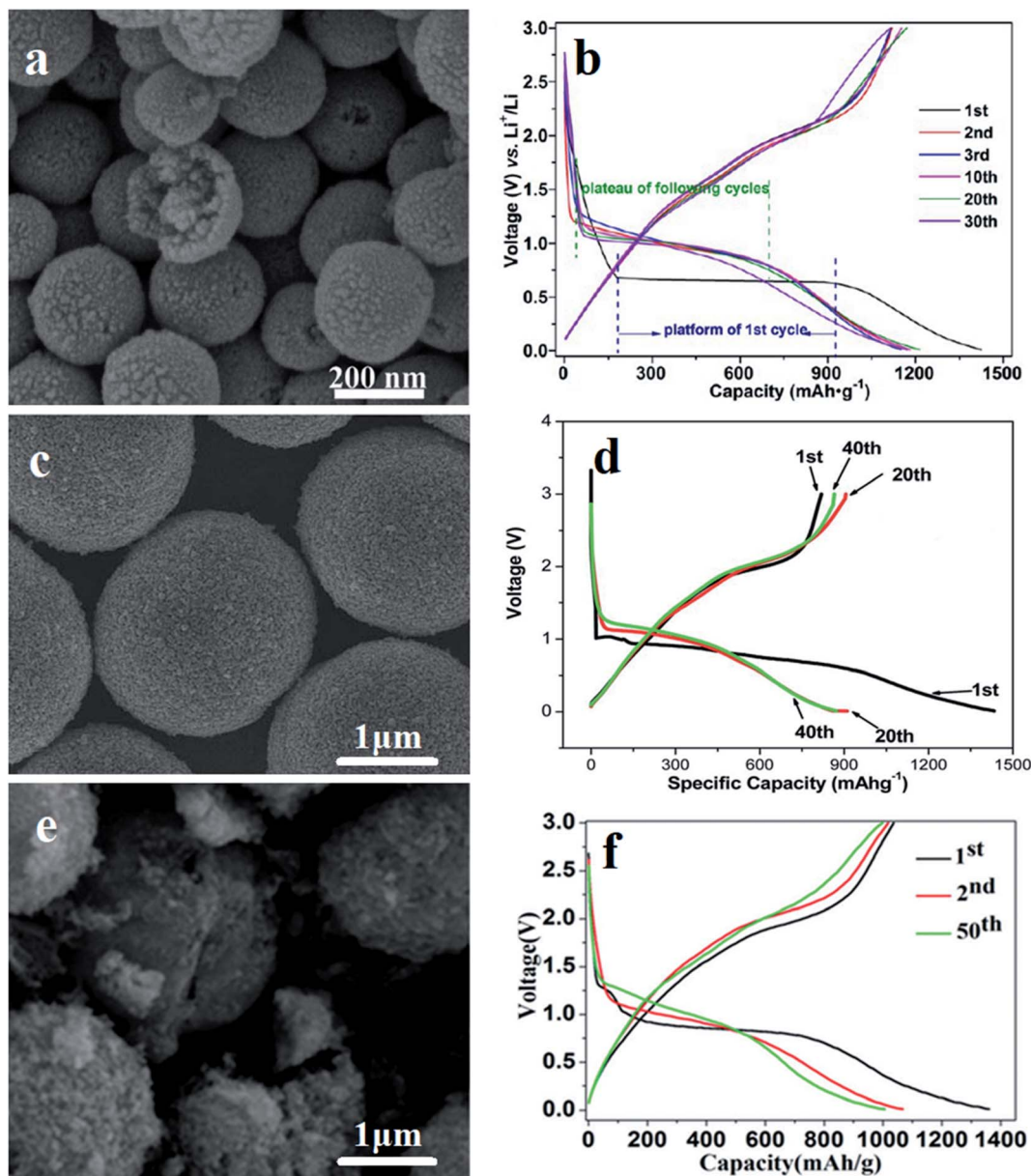


Fig. 4 Scanning electron microscopy images (SEM) and galvanostatic charge–discharge profiles (GCD) of yolk–shell MnCo_2O_4 . SEM images of (a) hollow MnCo_2O_4 submicrospheres. (c) Hierarchical porous MnCo_2O_4 yolk–shell microspheres and (e) spherical yolk–shell MnCo_2O_4 powders. GCD curves of (b) hollow MnCo_2O_4 submicrospheres, (d) hierarchical porous MnCo_2O_4 yolk–shell microspheres and (f) spherical yolk–shell MnCo_2O_4 powders. (a) and (b) adapted with permission from ref. 120. Copyright © 2014, American Chemical Society. (c and d) adapted with permission from ref. 121. Copyright © Marketplace™, Royal Society of Chemistry. (e and f) adapted with permission from ref. 124. Copyright © Marketplace™, Royal Society of Chemistry.

and carbon materials have been reported.^{152,160–163} A peanut shaped MnCo_2O_4 which is encapsulated by multi-walled carbon nanotubes (MCO/MWCNTs) was synthesized through a solvothermal method. The batteries exhibited a discharge capacity of 8849 mA h g^{-1} with a restricted voltage of 2 V at 100 mA g^{-1} and a cycle life of 120 times at 100 mA g^{-1} with a limited capacity of 500 mA h g^{-1} .¹⁶⁴

3.2.4. Other metal–air batteries. MnCo_2O_4 electrodes can be prepared as active materials for different metal–air batteries. Ishihara *et al.*¹⁶⁵ studied ORR/OER on mesoporous spinels for

Zn–air rechargeable batteries. The MnCo_2O_4 spinel showed a surface area of $108 \text{ m}^2 \text{ g}^{-1}$ and an average pore size of 2 nm , providing a decrease of overpotential for the ORR/OER in Zn–air batteries, which showed a stable discharge potential and capacity at 1.05 V and 700 mA h g^{-1} , respectively.

Carbonaceous materials and heteroatom doped-carbon materials were also mixed with MnCo_2O_4 due to their intrinsic advantages as ORR catalysts, such as higher surface area and electrochemical stability. Chandrappa *et al.*¹⁶⁶ reported a composite formed by combining MnCo_2O_4

Table 2 Performances reported for MnCo₂O₄-based metal ion batteries^a

Battery type	Material type	Material	Initial discharge (mA h g ⁻¹)	Potential window (V vs.)	Reversible capacity (Nth) mA h g ⁻¹	Stability (cycle numbers)	Ref.
Lithium ion batteries (LIBs)	Pristine MnCo ₂ O ₄	MnCo ₂ O ₄ yolk-shell microspheres	1035.8 at 0.1C	0.01–3 Li/Li ⁺	691.3 (500) at 1C	—	124
		Core-shell ellipsoidal MnCo ₂ O ₄	1433.3 at 0.1 A g ⁻¹	0.01–3 Li/Li ⁺	750 (70) at 100 mA g ⁻¹	—	128
		Micro-octahedral MnCo ₂ O ₄	1438 at 300 mA g ⁻¹	0.01–3 Li/Li ⁺	720.4 (200) at 300 mA g ⁻¹	88% (200 cycles)	110
		MnCo ₂ O ₄ nanoflakes	1795 at 50 mA g ⁻¹	0.01–3 Li/Li ⁺	925 (50) at 100 mA g ⁻¹	—	109
		MnCo ₂ O ₄ microspheres	1473 at 60 mA g ⁻¹	0.01–3 Li/Li ⁺	533 (200) at 400 mA g ⁻¹	—	106
		MnCo ₂ O ₄ cubic microcrystals	1443 at 100 mA g ⁻¹	0.01–3 Li/Li ⁺	—	28% (100 cycles)	104
		MnCo ₂ O ₄ needle-shaped	1326 at 60 mA g ⁻¹	0.01–3 Li/Li ⁺	368 (50) at 60 mA g ⁻¹	55% (50 cycles)	107
		MnCo ₂ O ₄ hollow spheres	1561 at 200 mA g ⁻¹	0.01–3 Li/Li ⁺	1023 (200) at 60 mA g ⁻¹	—	122
		MnCo ₂ O ₄ hollow microspheres	1119 at 400 mA g ⁻¹	0.01–3 Li/Li ⁺	800 (100) at 100 mA g ⁻¹	—	120
		MnCo ₂ O ₄ quasi-hollow microspheres	1473 at 200 mA g ⁻¹	0.01–3 Li/Li ⁺	610 (100) at 400 mA g ⁻¹	—	123
		MnCo ₂ O ₄	900 at 60 mA g ⁻¹	0.005–3 Li/Li ⁺	816 (50) 60 mA g ⁻¹	—	111
		MnCo ₂ O ₄ microspheres	1425.8 at 400 mA g ⁻¹	0.005–3 Li/Li ⁺	1033.3 (200)/400 mA g ⁻¹	74.2% (200 cycles)	105
		Dumbbell-shaped porous MnCo ₂ O ₄	2073 at 200 mA g ⁻¹	0.01–3 Li/Li ⁺	955(180) at 200 mA g ⁻¹	46% (180 cycles)	127
		Erythrocyte like MnCo ₂ O ₄	1538 at 200 mA g ⁻¹	0.01–3 Li/Li ⁺	960 (100) at 200 mA g ⁻¹	—	112
		Mesoporous MnCo ₂ O ₄ microflowers	1465.1 at 100 mA g ⁻¹	0.01–3 Li/Li ⁺	732 (50) at 100 mA g ⁻¹	—	125
		MnCo ₂ O ₄ nanospheres	1184.8 at 400 mA g ⁻¹	0.01–3 Li/Li ⁺	749.1 (50) at 200 mA g ⁻¹	89.8% (50 cycles)	108
		Porous MnCo ₂ O ₄	1750.0 at 400 mA g ⁻¹	0.01–3 Li/Li ⁺	690.1 (100) at 0.5C	—	114
		Flake-like MnCo ₂ O ₄	1460 at 100 mA g ⁻¹	0.01–3 Li/Li ⁺	952 (100) at 100 mA g ⁻¹	89% (100 cycles)	35
		MnCo ₂ O ₄ nanosheets	3.9 mA h cm ⁻² at 800 μA cm ⁻²	0.01–3 Li/Li ⁺	3.0 mA h cm ⁻² (60) at 800 μA cm ⁻²	—	116
		MnCo ₂ O ₄ -metal oxide composite	MnCo ₂ O ₄ -metal oxide composite	Porous MnCo ₂ O ₄ nanosheets	1044 at 0.2 A g ⁻¹	0.01–3 Li/Li ⁺	848 (200) at 0.2 A g ⁻¹
Porous MnCo ₂ O ₄ microspheres	1034 at 1000 mA g ⁻¹			0.01–3 Li/Li ⁺	740 (1000) at 1000 mA g ⁻¹	—	115
Yolk-shell MnCo ₂ O ₄ microspheres	1445.1 at 0.2 A g ⁻¹			0.01–3 Li/Li ⁺	860 (40) at 0.2 A g ⁻¹	—	121
MnCo ₂ O ₄	1220 at 0.1C			0.1–3 Li/Li ⁺	907 (50) at 0.5C	90% (50 cycles)	146
MnCo ₂ O ₄ nanotubes	1211.9 at 0.5 A g ⁻¹			0.01–3 Li/Li ⁺	701.4 (320) at 500 mA g ⁻¹	—	147
Porous hydrangea-like MnCo ₂ O ₄	1232 at 0.1 A g ⁻¹			0.01–3 Li/Li ⁺	930 (100) at 0.1 A g ⁻¹	87% (100 cycles)	126
CoO/MnCo ₂ O _{4.5} nanorods	1183 at 200 mA g ⁻¹			0.01–3 Li/Li ⁺	1030 (120) at 200 mA g ⁻¹	87% (120 cycles)	118
MnCo ₂ O ₄ @NC@MnO ₂	1380 at 500 mA g ⁻¹			0.01–3 Li/Li ⁺	894 (120) at 500 mA g ⁻¹	—	136
NiO-MnCo ₂ O ₄ -Ni ₆ MnO ₈	1284 at 30 mA g ⁻¹			0.01–3 Li/Li ⁺	779 (120) at 1C	—	129
Co ₃ O ₄ -MnCo ₂ O ₄ powder, 20–50 nm	1781 at 50 mA g ⁻¹			0.01–3 Li/Li ⁺	1250 (200) at 1000 mA g ⁻¹	68.2% (200 cycles)	119
MnCo ₂ O ₄ -TiO ₂ microspheres	1396.9 at 100 mA g ⁻¹			0.01–3 Li/Li ⁺	1271 (200) at 100 mA g ⁻¹	91% (200 cycles)	135
Porous MnCo ₂ O ₄ @MnO ₂	1927.8 at 100 mA g ⁻¹			0.0–3 Li/Li ⁺	1162.8 (200) at 1 A g ⁻¹	96% (200 cycles)	134
NiO-MnCo ₂ O ₄ microspheres	1206 at 200 mA g ⁻¹			0.01–3 Li/Li ⁺	846 (50) at 200 mA g ⁻¹	—	130
3D sandwich-shaped graphene-based MnCo ₂ O ₄ hollow spheres	1244 at 200 mA g ⁻¹			0.01–3 Li/Li ⁺	703 (100) at 200 mA g ⁻¹	80% (100 cycles)	131
MnCo ₂ O ₄ -carbon based composites	MnCo ₂ O ₄ -carbon based composites	Graphene-like 2D spinel MnCo ₂ O ₄	1157.7 at 0.2 A g ⁻¹	0.01–3 Li/Li ⁺	780 (200) at 0.2 A g ⁻¹	—	139
		MnCo ₂ O ₄ nanoparticles embedded in graphene sheets	1350 at 100 mA g ⁻¹	0.01–3 Li/Li ⁺	584.3 (250) at 2000 mA g ⁻¹	92.3% (250 cycles)	138
		MnCo ₂ O ₄ @carbon cloth	1886.2 at 1 A g ⁻¹	0.01–3 Li/Li ⁺	1289 (200) at 1 A g ⁻¹	—	117
		MnCo ₂ O ₄ /rGO composite	1657 at 0.1 A g ⁻¹	0.01–3 Li/Li ⁺	791 (100) at 0.2 A g ⁻¹	74.1% (100 cycles)	142
		MnCo ₂ O ₄ /C	1284.5 at 1 A g ⁻¹	0.01–3 Li/Li ⁺	978 (800) at 1 A g ⁻¹	—	148
		MWCNT composite	1471 at 946 mA g ⁻¹	0.005–3 Li/Li ⁺	871 (30) at 60 mA g ⁻¹	—	140
		MnCo ₂ O ₄ /polypyrrole	1398 at 200 mA g ⁻¹	0.01–3 Li/Li ⁺	910 (100)/200 mA g ⁻¹	—	141
		Flower-like MnCo ₂ O ₄ @PANI-rGO	—	0.01–3 Li/Li ⁺	745 (1050)/500 mA g ⁻¹	—	143

Table 2 (Contd.)

Battery type	Material type	Material	Initial discharge (mA h g ⁻¹)	Potential window (V vs.)	Reversible capacity (Nth) mA h g ⁻¹	Stability (cycle numbers)	Ref.
Sodium ion batteries	Other MnCo ₂ O ₄ -based composite materials	Mn _{0.4} Ni _{0.6} Co ₂ O ₄ nanowires MnCo ₂ O ₄ porous nanospheres@N-doped carbon	1054 at 0.1 A g ⁻¹ 1099.9 at 1 A g ⁻¹	0.01–3 Li/Li ⁺ 0.01–3 Li/Li ⁺	706 (200) at 500 mA g ⁻¹ 883.3 (500) at 1 A g ⁻¹	98% (200 cycles)	132 137
	—	Ni-doped MnCo ₂ O ₄ submicron-spheres Mesoporous Ni-doped MnCo ₂ O ₄ hollow nanotubes	1849 at 0.2 A g ⁻¹ 340 at 0.1 A g ⁻¹	0.01–3 Li/Li ⁺ 0.01–3 Na/Na ⁺	174.7 (2000) at 5 A g ⁻¹ 109 (11 000) at 1 A g ⁻¹	— 81% (11 000 cycles)	133 144
—	MnCo ₂ O ₄ -carbon based composites	Flower-like MnCo ₂ O ₄ MnCo ₂ O ₄ /nanographene	697 at 25 mA g ⁻¹ 1120 at 0.05 A g ⁻¹	0.01–3 Na/Na ⁺ 0.01–3 Na/Na ⁺	244 (40) at 50 A g ⁻¹ 541.2 (200) at 0.05 A g ⁻¹	77.1% (40 cycles)	145 77

^a rGO = reduced graphene oxide, MWCNT = multi wall carbon nanotube, PANI = polyaniline, and NC = N-doped carbon.

nanospheres with graphene sheets (MCO/GS) as a bifunctional cathode catalyst for Zn–air batteries. The electrochemical measurements revealed a unique small charge–discharge overpotential, cycling stability and higher rate capability than a bare MCO catalyst. Carbon coated MnCo₂O₄ nanowires (MnCo₂O₄@C) were also used as a bifunctional oxygen catalyst for rechargeable Zn–air batteries. The authors recorded an excellent electrochemical performance and improved cycling stability, with an onset potential of 0.92 V and current retention rate of 99% within 10 000 s at 0.80 V vs. RHE.¹⁶⁷ Besides Zn–air batteries,^{166–169} Na–air devices have also been reported in the literature.^{170,171} Table 3 summarizes the performance of different cells coupled with different metal–air batteries of electrodes based on MnCo₂O₄.

4. MnCo₂O₄-based electrocatalysts for energy conversion and storage

4.1. ORR catalysts in energy storage

As already highlighted in the previous topics, the development of high-performance electrocatalysts is essential for achieving high-performance energy devices, especially catalysts for oxygen reactions (OER and ORR) due to the sluggish reaction kinetics, which often requires a large overpotential to sustain a reasonable rate of electrode reactions.¹⁷² In fact, the design and optimization of catalysts for the ORR/OER is of fundamental importance for the development of more efficient and competitive energy storage devices, such as for metal–air batteries¹⁷³ and proton exchange membrane fuel cells (PEMFCs).¹⁷⁴

Currently, Ir and/or Ru based oxides and Pt-based materials are the most widely used catalysts for the OER and ORR, respectively. However, the high cost, scarcity, and poor bifunctional activity of precious metals greatly hinder their industrial application on a large scale.¹⁷⁵ To solve these disadvantages, intensive efforts have been devoted to development of noble metal-free oxygen reaction catalysts with low cost and high activity in the past decades,¹⁷⁶ especially for ORR catalysts. Among these reported noble metal-free ORR catalysts or bifunctional oxygen electrocatalysts, MnCo₂O₄ and MnCo₂O₄-derived composites show great potential as electrocatalysts because of their high intrinsic activity, and the corresponding activities can be further tuned through their phase and composition.¹⁷⁷

In fact, based on Table 4, it is possible to perceive important and well-known strategies that have been employed in the design of electrocatalysts containing MnCo₂O₄ for the ORR, as for example: (1) active site engineering, obtained through the control of size, morphology and defects, as well as the crystal-line phase, in order to maximize the density of active sites,^{3,178} and (2) conductivity optimization, obtained especially by doping with hetero-atoms and/or by formation of composites with conducting materials.^{3,178,179}

As an excellent example of the active site engineering strategy, Yang *et al.*¹⁸⁰ successfully reported a facile precursor pyrolysis method to prepare porous spinel cobalt manganese oxides with tunable size, shape, chemical composition and



Fig. 5 Scanning electron microscopy images (SEM) of different morphologies of MnCo_2O_4 . SEM images of (a) MnCo_2O_4 nanowires, (b) single-wall MnCo_2O_4 nanotubes and (c) MnCo_2O_4 nanospheres. Fig. 1a adapted with permission from ref. 53. Copyright © 2017, American Chemical Society. Fig. 1b, adapted with permission from ref. 154. Copyright © Marketplace™, Royal Society of Chemistry. Fig. 1c adapted with permission from ref. 155. Copyright © Marketplace™, Royal Society of Chemistry.

crystalline structure *via* a facile precursor pyrolysis method (Fig. 6a). The capping agent and reaction temperature in the reaction were found to be crucial in the formation of porous

spinel cobalt manganese oxides from cubic Co_2MnO_4 nanorods (c-CMO NRs) to tetragonal CoMn_2O_4 microspheres (t-CMO MSs) and tetragonal CoMn_2O_4 cubes (t-CMO CBs).

Table 3 Performances reported for MnCo_2O_4 -based metal–air batteries

Type	Cathodes	Initial discharge (mA h g^{-1})	Discharge voltage (V)	Charge voltage (V)	Overpotential ^a (V)	Stability (cycle numbers)	Ref.
Na air battery	$\text{Co}_3\text{O}_4@\text{MnCo}_2\text{O}_{4.5}$ nanocubes	8400 at 500 mA g^{-1}	2.3	2.75	0.45	(135 cycles)	171
	dp- $\text{MnCo}_2\text{O}_4/\text{N-rGO}$	—	2.75	3.14	0.39	(25 cycles)	170
	Ni-doped hollow nanotubes	340.5 at 0.1 A g^{-1}	—	—	—	81% (11 000 cycles)	144
Zn air battery	MnCo_2O_4 nanofibers	125 at 10 mA cm^{-2}	—	—	1.23	(500 cycles)	168
	MnCo_2O_4 nanoparticles embedded in nitrogen-doped macroporous carbon nanofiber arrays	—	—	—	0.55	(100 cycles)	169
Li air battery	$\text{MnCo}_2\text{O}_4@\text{C}$ nanowires	—	—	—	0.89	—	167
	$\text{MnCo}_2\text{O}_4@\text{Ni}$	10 520 at 100 mA g^{-1}	2.79	—	0.65	1000 mA h g^{-1} (119 cycles)	150
	Nanowires	12 919 at 0.1 mA cm^{-2}	2.92	3.46	0.54	1000 mA h g^{-1} (144 cycles)	153
	Microspheres	2809.1 at 500 mA g^{-1}	2.7	3.9	—	1000 mA h g^{-1} (50 cycles)	156
	P-Doped hierarchical porous carbon	13 150 at 200 mA g^{-1}	2.75	4.0	—	1000 mA h g^{-1} (200 cycles)	157
	$\text{Ti}_4\text{O}_7/\text{MnCo}_2\text{O}_4$	5400 at 100 mA g^{-1}	2.85	3.6	0.75	500 mA h g^{-1} (100 cycles)	158
	MnCo_2O_4 nanospheres	8518 at 100 mA g^{-1}	2.86	—	0.85	1000 mA h g^{-1} (20 cycles)	155
	MnCo_2O_4 nanorods	1334 at 0.1 mA cm^{-2}	2.61	4.10	—	500 mA h g^{-1} (40 cycles)	151
	$\text{MnCo}_2\text{O}_4/\text{graphene}$	3784 at 100 mA g^{-1}	2.95	3.75	~0.8	1000 mA h g^{-1} (40 cycles)	162
	Peanut shaped $\text{MnCo}_2\text{O}_4/\text{MWCNTs}$	8849 at 100 mA g^{-1}	—	—	—	500 mA h g^{-1} (120 cycles)	164
	$\text{MnCo}_2\text{O}_4/\text{graphene}$	10 092 at 100 mA g^{-1}	2.9	3.7	0.8	1000 mA h g^{-1} (250 cycles)	161
	$\text{MnCo}_2\text{O}_4@\text{carbon cloth}$	7238 at 200 mA g^{-1}	—	—	1.46	500 mA h g^{-1} (108 cycles)	160
	$\text{MnCo}_2\text{O}_4\text{-graphene}$	11 092.1 at 200 mA g^{-1}	—	—	—	1000 mA h g^{-1} (35 cycles)	163
Double-wall MnCo_2O_4 nanotubes	8100 at 100 mA g^{-1}	2.77	4.14	1.37	1000 mA h g^{-1} (278 cycles)	154	
$\text{MnCo}_2\text{O}_4/\text{MoO}_2@\text{Ni}$ nanosheets	4210 at 200 mA g^{-1}	—	—	—	0.75 (400 cycles)	159	
MnCo_2O_4 nanowires	8364 at 200 mA g^{-1}	—	—	—	0.823 (167 cycles)	152	

^a The overpotential was calculated based on the difference of discharge–charge voltage plateaus. rGO = reduced graphene oxide, MWCNT = multi wall carbon nanotube, and C = carbon.

Table 4 Catalytic activity parameters of recently reported ORR MnCo₂O₄-based electrocatalysts^a

ORR catalysts	Incorporated or doping atom	Substrate	E_{ORR} onset potential (V vs. RHE)	Half wave potential (V vs. RHE)	E_{ORR} at -3 mA cm ⁻¹ (V vs. RHE)	E_{ORR} at 10 mA cm ⁻¹ (V vs. RHE)	ΔE $E_{\text{ORR}}-E_{\text{ORR}}$ vs. RHE	Current density (mA cm ⁻¹)	Tafel slope (mV dec ⁻¹)	Average electron transfer number (n)	Stability (h)	pH condition	Ref.
MCO-700	—	GCE	—	—	—	—	—	6.69 mA cm ⁻¹	—	3.2–3.5	–16.66	0.1 M KOH	189
CMO-3.9/CNT	CNT	GCE	—	0.86	—	1.61	—	2.90 mA cm ⁻¹ at 0.7 V	65–126	3.98	94%	0.1 M KOH	190
MnCo ₂ O ₄	—	—	0.88	0.77	—	—	—	—	—	—	87%	0.1 M KOH	167
MnCo ₂ O ₄ @C	Carbon	—	0.92	0.80	—	1.66	0.89 ^d	—	—	3.61	99%	0.1 M KOH	167
MnCo ₂ O ₄ /C	Vulcan carbon	GCE	—	0.76	—	~1.74	—	—	~61	3.51	–8.33	0.1 M KOH	184
MnCo ₂ O ₄ /C nanosheets	Porous C nanosheets	GCE	0.945	0.767	—	—	—	—	—	3.82	72.5%	0.1 M KOH	183
MnCo ₂ O ₄	—	GCE	~0.83 ^a	1.12	0.66	—	—	–2.30 mA cm ⁻¹ at 0.36 V	–142.2	—	2.77	0.1 M KOH	20
MnCo ₂ O ₄ -rGO	rGO	GCE	~0.89 ^a	1.11	0.77	—	—	–3.33 mA cm ⁻¹ at 0.36 V	–150.1	3.8	–2.22	0.1 M KOH	20
MCO	—	GCE	–0.165	–0.225	–0.647	0.840	1.487	—	145	$n > 3$	—	0.1 M KOH	21
MCO + NS-MCS	NS-MCS	GCE	–0.112	–0.186	–0.221	0.817	1.038	–4.60 mA cm ⁻¹ at –1.0 V	131	$n > 3$	—	0.1 M KOH	21
MCO/NS-MCS	NS-MCS	GCE	–0.079	–0.160	–0.186	0.774	0.960	–5.03 mA cm ⁻¹ at –1.0 V	124	3.64–3.88	82.3%	0.1 M KOH	21
MnCo ₂ O ₄ at 500 °C	—	GCE	0.81 ^a	0.58	—	—	—	—	—	—	5.55	0.1 M KOH	22
N-MWCNT-MnCo ₂ O ₄ at 500 °C	N-MWCNT	GCE	0.83 ^a	0.86	0.75	—	—	—	—	3.9	–20	0.1 M KOH	22
N-MWCNT-MnCo ₂ O ₄ at 500 °C	N-MWCNT	GCE	0.86 ^a	0.60	—	—	—	—	—	—	—	0.1 M KOH	22
MCO	—	GCE	—	—	<0.1	>1.9	>2	—	—	—	—	0.1 M KOH	177
MCO + NCNTs	NCNTs	GCE	—	—	0.70	1.74	1.04	—	—	—	—	0.1 M KOH	177
MCO@NCNTs	NCNTs	GCE	—	—	0.76	1.70	0.94	—	–96 and –125	3.9	—	0.1 M KOH	177
MnCo ₂ O ₄ /CNT	CNT	GCE	—	—	—	—	—	—	—	3.75	—	0.1 M KOH	191
MnCo ₂ O ₄ /N,S-CNT	N,S-CNT	GCE	—	—	—	—	—	—	—	3.83	72%, 5	0.1 M KOH	191
MnCo ₂ O ₄ /rGO	rGO	GCE	0.94	0.78	—	—	—	—	75.4	3.90	—	0.1 M KOH	185
MnCo ₂ O ₄ /3D-G	3D-G	GCE	0.98	0.81	—	—	—	—	68.5	3.96	79.84%, 60	0.1 M KOH	185

Table 4 (Contd.)

ORR catalysts	Incorporated or doping atom	Substrate	E_{ORR} onset potential (V vs. RHE)	Half wave potential (V vs. RHE)	E_{ORR} at -3 mA cm^{-2} (V vs. RHE)	E_{ORR} at 10 mA cm^{-2} (V vs. RHE)	ΔE $E_{\text{OER}}-E_{\text{ORR}}$ (V vs. RHE)	Current density (mA cm^{-2})	Tafel slope (mV dec^{-1})	Average electron transfer number (n)	Stability (h)	pH condition	Ref.
MnCo ₂ O ₄ /CNTs	CNTs	GCE	0.93	0.74	—	—	—	84.6	—	3.81	—	0.1 M KOH	185
MnCo ₂ O ₄ /C	C	GCE	0.92	0.72	—	—	—	87.4	—	3.76	—	0.1 M KOH	185
MnCo ₂ O ₄	—	—	0.865	0.552	—	—	—	—	—	—	—	0.1 M KOH	186
MnCo ₂ O ₄ + N-C	N-C	—	0.918	0.780	—	—	—	—	—	—	—	0.1 M KOH	186
MnCo ₂ O ₄ /N-C	N-C	—	0.943	0.795	—	—	—	—	—	3.50–3.83	89.68% at 0.2 V	0.1 M KOH	186
CoMn/pNGr (2 : 1)	pNGr	GCE	0.94 ^a , 0.9 ^a	0.791	—	—	—	74	—	3.98	2.77	0.1 M KOH	192
CoMn/pNGr (1 : 1)	pNGr	GCE	0.9 ^a	0.726	—	—	—	—	—	3.66	—	0.1 M KOH	192
CoMn/pNGr (1 : 2)	pNGr	GCE	0.92 ^a	0.734	—	—	—	—	—	3.46	—	0.1 M KOH	192
MnCo ₂ O ₄ /NGr	NGr	GCE	0.86 ^a	0.648	—	—	—	—	—	—	—	0.1 M KOH	192
MnCo ₂ O ₄ /N-rmGO	N-rmGO	GCE	0.95 ^a , ^c	—	—	—	—	36 ^c	—	~3.9 ^c	96.5%	1 M KOH	188
MnCo ₂ O ₄ + N-rmGO	N-rmGO mixture	GCE	0.91 ^a , ^c	—	—	—	—	—	—	~3.7 ^c	5.55	1 M KOH	188
Mesoporous MnCo ₂ O ₄	—	GCE	0.95 ^a	—	0.80	1.63	0.83	—	—	3.94	85% 10	0.1 M KOH	182
m-MnCo ₂ O ₄	—	GCE	-0.04	—	—	—	—	-95	—	3.96	87% 95	0.1 M KOH	181
MnCo ₂ O ₄ /C	C	GCE	0.93 ^c	0.76 ^c	—	1.52 ^c	0.59 ^c	68/207 ^c	—	3.92 ^c	-24	1 M KOH	193
dp-MnCo ₂ O ₄ /CNT	CNT	GCE	-0.11 ^b	—	—	—	—	106	—	~4.0	—	0.1 M KOH	194
dp-MnCo ₂ O ₄ /N-rGO	N-rGO	GCE	-0.09 ^b	—	—	—	—	65	—	~4.0	—	0.1 M KOH	194
MnCo ₂ O ₄	—	GCE	0.84	0.59	0.55	1.77	1.22	78.8	—	2.5–3.7	—	0.1 M KOH	187
CMO/20N-rGO	N-rGO	GCE	0.93	0.79	0.77	1.68	0.91	50.8	—	3.9–4	86.3% 8	0.1 M KOH	187
NCNTs	NCNTs	GCE	—	—	—	—	—	—	—	3.4	—	0.1 M KOH	195
NCNT-500	NCNTs	GCE	—	—	—	1.495	—	—	—	3.8	—	0.1 M KOH	195
MnCo ₂ O ₃ /C	C	GCE	—	0.86 ^c	—	—	—	45 ^c	—	—	—	1 M KOH	196

Table 4 (Contd.)

ORR catalysts	Incorporated or doping atom	Substrate	E_{ORR} onset potential (V vs. RHE)	Half wave potential (V vs. RHE)	E_{ORR} at -3 mA cm $^{-2}$ (V vs. RHE)	E_{ORR} at 10 mA cm $^{-2}$ (V vs. RHE)	ΔE $E_{\text{ORR}} - E_{\text{ORR}}$ (V vs. RHE)	Current density (mA cm $^{-2}$)	Tafel slope (mV dec $^{-1}$)	Average electron transfer number (n)	Stability (h)	pH condition	Ref.
MnCo $_2$ O $_4$ /C	C	GCE	—	0.84 ^c	—	—	—	—	50 ^c	—	—, 10 000 cycles	1 M KOH	196
c-CMO NRs	—	GCE	0.9	0.72	—	—	—	5.9 mA cm $^{-2}$	—	3.9	95%, 2.77	0.1 M KOH	180
t-CMO MSs	—	GCE	0.89	0.70	—	—	—	5.5 mA cm $^{-2}$	—	~3.8	95%, 2.77	0.1 M KOH	180
t-CMO CBs	—	GCE	0.89	0.65	—	—	—	5.51 mA cm $^{-2}$	—	3.6	89%, 2.77	0.1 M KOH	180
MnCo $_2$ O $_3$ /CNF	CNF	GCE	-0.08 ^b	-0.21 ^b	—	—	1.04	—	—	~3.96	89%, 8.33	0.1 M KOH	197
D-AC@2Mn-4Co	D-AC	GCE	883	803	—	—	—	4.72 mA cm $^{-2}$ at 0.2 V	37.5	3.83	92.7%, 20 000	0.1 M KOH	198
Co $_2$ MnO $_4$	—	—	—	—	0.59	1.92	1.33	—	3.89	—	—, —	0.1 M KOH	199
Co $_3$ O $_4$ + Co $_2$ MnO $_4$	—	—	—	—	0.55	1.86	1.31	—	3.85	—	—, —	0.1 M KOH	199
Co $_3$ O $_4$ /Co $_2$ MnO $_4$	—	—	—	—	0.68	1.77	1.09	—	3.97	—	~94%, 2.77	0.1 M KOH	199

^a a = obtained by cyclic voltammetry, b = vs. Ag/AgCl, — = information not found in the paper, c = 1 M KOH, d = $\Delta E = |E_{j_{10}}| - |E_{j_{1/2}}|$, MCO/NS-MCS = cobalt spinel oxides supported on nitrogen and sulfur co-doped mesoporous carbon spheres, N-doped MWCNT = nitrogen-doped multi-walled carbon nanotube, N,S-CNT = N,S-doped carbon nanotubes, 3D-G = three-dimensional graphene, N-C = N-doped carbon, pNGr = N-doped porous graphene, D-AC = AC-based defective carbon, t-CMO CBs = tetragonal CoMn $_2$ O $_4$ cubes, tetragonal CoMn $_2$ O $_4$ microspheres, and c-CMO NRs = cubic Co $_2$ MnO $_4$ nanorods.

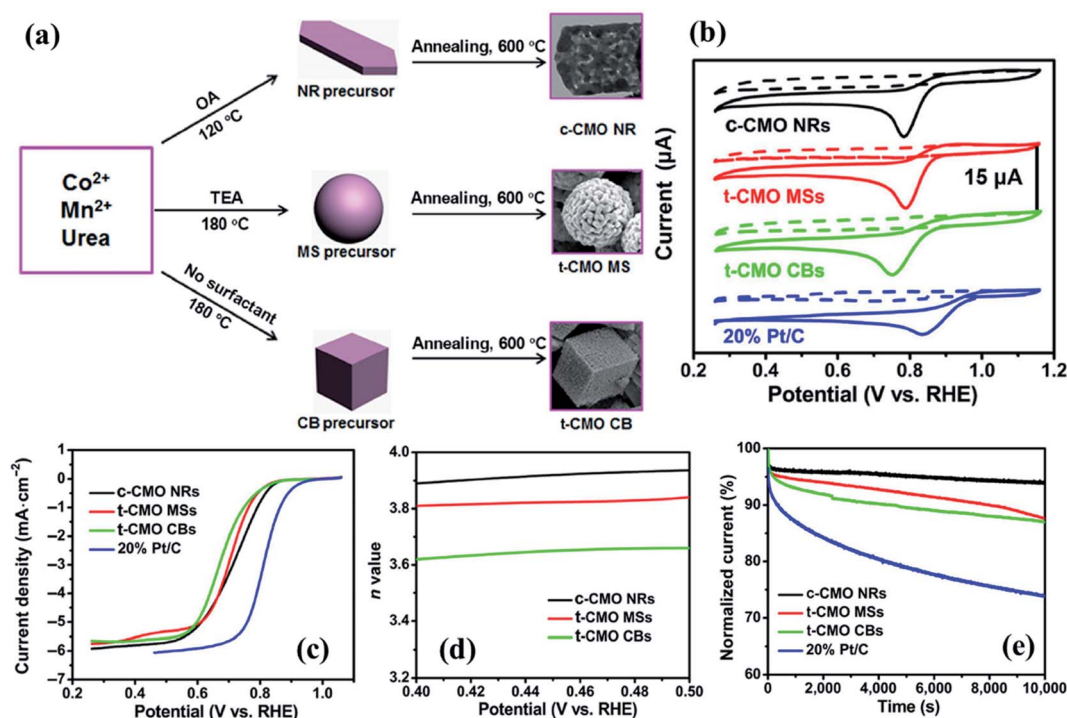


Fig. 6 (a) The synthetic process of different spinel $\text{Co}_x\text{Mn}_{3-x}\text{O}_4$. ORR data of the prepared CMOs in O_2 versus Ar-saturated 0.1 M KOH with a catalyst mass loading of 0.21 mg cm^{-2} . (b) Cyclic voltammetry curves of electrocatalysts in O_2 versus Ar-saturated 0.1 M KOH. (c) Linear sweep voltammograms of the electrocatalysts in 0.1 M KOH at 1600 rpm. (d) Electron transfer number n at different potentials. (e) Chronoamperometric responses (percentage of current retained versus operation time) of the different spinel CMOs and 20% Pt/C kept at 0.50 V vs. RHE in O_2 -saturated 0.1 M KOH. Reproduced with permission from ref. 180. Copyright © 2016, Tsinghua University Press and Springer-Verlag Berlin Heidelberg.

As illustrated in CVs (Fig. 6b) and polarization curves (Fig. 6c) of porous CMOs and 20% Pt/C, all the prepared spinel CMOs exhibited good ORR electrocatalytic activities, of which the c-CMO NRs showed a much more positive onset potential of 0.9 V and a half-wave potential of 0.72 V, which are very close values to those obtained by a commercial Pt/C. Furthermore, the n value of the c-CMO NRs in ORR electrocatalysis was calculated to be about 3.9 in the range of 0.45 and 0.60 V (Fig. 6d, which is in good agreement with a 4-electron oxygen reduction process) and demonstrated a desired durability with negligible degradation of their electrocatalytic activity after a continuous operation time of 10 000 seconds (Fig. 6e), which is much better than that of the commercial Pt/C electrocatalyst.¹⁸⁰

The active site engineering strategy has also been used in the development of a mesoporous MnCo_2O_4 electrode material.¹⁸¹ In one of these studies, Wang and co-workers¹⁸² reported a mesoporous bifunctional oxygen MnCo_2O_4 electrocatalyst synthesized through a spray-pyrolysis route (Fig. 7a), with Mn^{IV} in the surface and Mn^{III} in the bulk while Co^{II} was present both in the surface and bulk, as confirmed by X-ray near-edge structure (XANES) and XPS investigation. As a result, the MnCo_2O_4 exhibited both Co_3O_4 -like activity for the OER (Fig. 7b) and Mn_2O_3 -like performance for the ORR (Fig. 7c), with a potential difference between the ORR and OER of 0.83 V. According to the Koutecky–Levich (K–L) equation, the electron

transfer number (n) of MnCo_2O_4 was calculated to be 3.94 and after 10 h, the loss of current density for MnCo_2O_4 was only 15%, indicating higher stability of MnCo_2O_4 than Pt/C (Fig. 7e). Another advantage is that the electrode material can be obtained on a large-scale at a relatively low temperature with precise chemical control of the components. The prominent bifunctional activity shows that MnCo_2O_4 could be used in metal–air batteries and/or other energy devices, as confirmed by the home-built Zn–air battery used to study the bifunctional stability of mesoporous MnCo_2O_4 (Fig. 7e).¹⁸²

On the other hand, conductivity optimization by the formation of composites with conducting carbon materials has been the main strategy for preparing excellent electrocatalysts for the ORR. In fact, pure MnCo_2O_4 nanoparticles displayed certain ORR catalytic activity, but with a poor onset potential and peak potential.¹⁸³ In this context, among the most used carbon materials for this application, it is possible to highlight Vulcan carbons,¹⁸⁴ CNTs²² and graphene derivatives.²⁰

In one of these studies, Zhang *et al.*¹⁸⁵ designed a strategy to prepare MnCo_2O_4 on three-dimensional graphene (3D-G), as shown in Fig. 8. Typically, 3D-G (with multilayered structure of graphene) was synthesized using a coal tar pitch as the carbon source and nano MgO as the template (Fig. 8a). Then, spinel MnCo_2O_4 nanoparticles were *in situ* prepared and deposited on the inner walls of pores in the 3D-G by a facile hydrothermal method, resulting in the $\text{MnCo}_2\text{O}_4/3\text{D-G}$ composite.¹⁸⁵

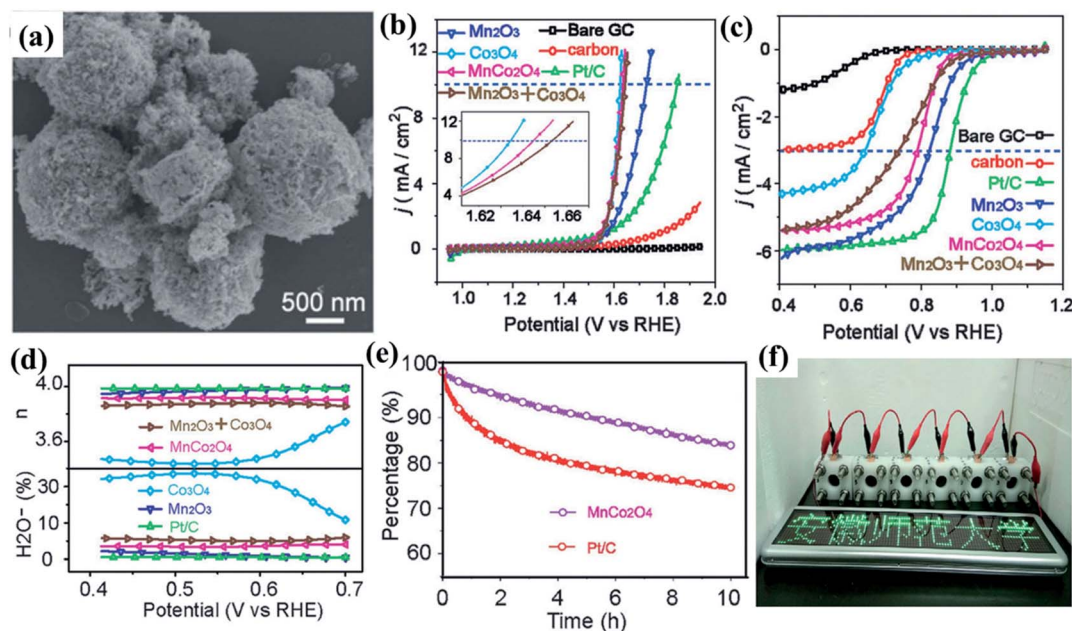


Fig. 7 (a) SEM of MnCo_2O_4 ; (b) OER polarization curves of catalysts at 1600 rpm; (c) ORR polarization curves of catalysts at 1600 rpm; (d) percentage of peroxide and electron numbers (n) of Co_3O_4 , Mn_2O_3 , MnCo_2O_4 , Pt/C, and the physical mixture of Mn_2O_3 and Co_3O_4 . (e) Chronoamperometric measurements of MnCo_2O_4 and Pt/C at -0.3 V (vs. Ag/AgCl) in O_2 -saturated 0.1 M KOH at 1600 rpm. (f) A green light emitting diode (LED) panel powered by six Zn–air batteries (containing MnCo_2O_4). Reproduced with permission from ref. 182. Copyright © 2017 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim University Press and Springer-Verlag Berlin Heidelberg.

Surprisingly, the $\text{MnCo}_2\text{O}_4/3\text{D-G}$ catalyst showed an onset potential of 0.98 V (vs. RHE) and the half-wave potential was 0.81 V (vs. RHE) in a solution of 0.1 M KOH (Fig. 8b), which was clearly superior to those of 20 wt% Pt/C (0.97 V, 0.80 V), $\text{MnCo}_2\text{O}_4/\text{rGO}$ (0.94 V, 0.78 V), $\text{MnCo}_2\text{O}_4/\text{CNTs}$ (0.93 V, 0.74 V), and $\text{MnCo}_2\text{O}_4/\text{C}$ (0.92 V, 0.72 V).¹⁸⁵ In addition, the electron transfer number was 3.96 at 0.4 V (vs. RHE), and its catalyzed

ORR mainly follows a four-electron process (Fig. 8c), indicating that the $\text{MnCo}_2\text{O}_4/3\text{D-G}$ catalyst possesses superior selectivity for the ORR process. Besides that, $\text{MnCo}_2\text{O}_4/3\text{D-G}$ showed the lowest Tafel slope of 68.5 mV dec^{-1} compared to those of Pt/C (70.2 mV dec^{-1} of 20 wt%), $\text{MnCo}_2\text{O}_4/\text{rGO}$ (75.4 mV dec^{-1}), $\text{MnCo}_2\text{O}_4/\text{CNTs}$ (84.6 mV dec^{-1}) and $\text{MnCo}_2\text{O}_4/\text{C}$ (87.4 mV dec^{-1}) (Fig. 8d), and the durability test demonstrated that the

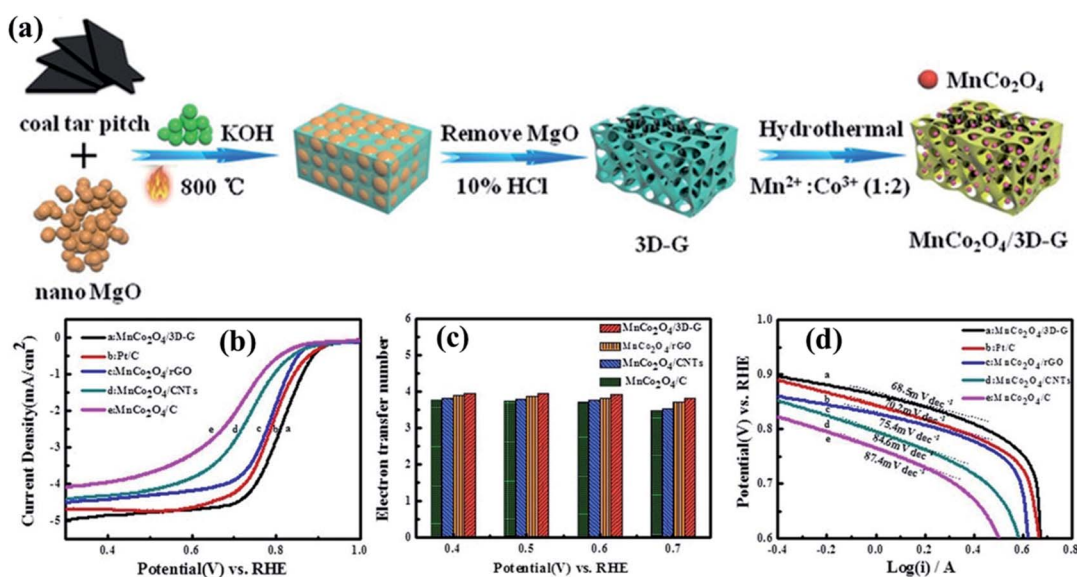


Fig. 8 (a) The synthesis route to the $\text{MnCo}_2\text{O}_4/3\text{D-G}$ catalyst. (b) LSV curves of the different catalysts. (c) Electron transfer number per oxygen molecule of the different catalysts at different potentials. (d) Tafel slopes of the electrode assemblies fabricated with different catalysts. Reproduced with permission from ref. 185. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

$\text{MnCo}_2\text{O}_4/3\text{D-G}$ catalyst has a much better durability than commercial Pt/C.¹⁸⁵ This work shows that the preparation of composites with carbonaceous materials is really an inspiring strategy to prepare high performance electrocatalysts for the development of fuel cells.

It is important to highlight that results as promising as those obtained in the work by Zhang *et al.*¹⁸⁵ were obtained by forming composites (conductivity optimization strategy) with conductive carbonaceous materials, applying the active site engineering strategy to the catalytic nanocarbon sites of these composites. In this combination of strategies, N and S-doped carbonaceous materials have been intensively studied,²¹ for example, Fu and co-workers¹⁸⁶ successfully prepared composed of N-doped carbon (N-C) and MnCo_2O_4 NPs for the ORR ($\text{MnCo}_2\text{O}_4/\text{N-C}$), with an ORR onset potential of 0.943 V, ORR half-wave potential of 0.795 V, synthesized by pyrolyzing the mesoporous-silica-protected zeolitic imidazolate framework-8 (ZIF-8) and etching, followed by a facile hydrothermal procedure (Fig. 9a). The superior performance of $\text{MnCo}_2\text{O}_4/\text{N-C}$ was

attributed to its porous structure and large surface area, N-doping effect, small size MnCo_2O_4 NPs and synergistic effects between the doped active species.¹⁸⁶ Based on the values of onset and half-wave potentials shown in Table 1, it is possible to infer that the $\text{MnCo}_2\text{O}_4/\text{N-C}$ reported by Fu *et al.*¹⁸⁶ presented slightly better performance than other composites containing N-doped carbonaceous materials, such as N-MWCNT- MnCo_2O_4 (ORR onset potential of 0.86 V, ORR half-wave potential of 0.75 V),²² and CMO/20N-rGO (ORR onset potential of 0.93 V, ORR half-wave potential of 0.79 V).¹⁸⁷

Using a slightly different approach, Liang *et al.*¹⁸⁸ developed hybrid composites through direct NP nucleation and growth on nitrogen doped-reduced graphene oxide (N-rmGO) sheets and Mn substitution of spinel Co_3O_4 NPs (average size of ~ 5 nm) for the ORR under alkaline conditions (Fig. 9b), as confirmed by the SEM (Fig. 9c) and TEM (Fig. 9d) images, as well as by the HRTEM images, showing the lattice fringes of the nanocrystals, consistent with the MnCo_2O_4 crystal structure (Fig. 9e). This method results in covalent coupling between oxide NPs and N-

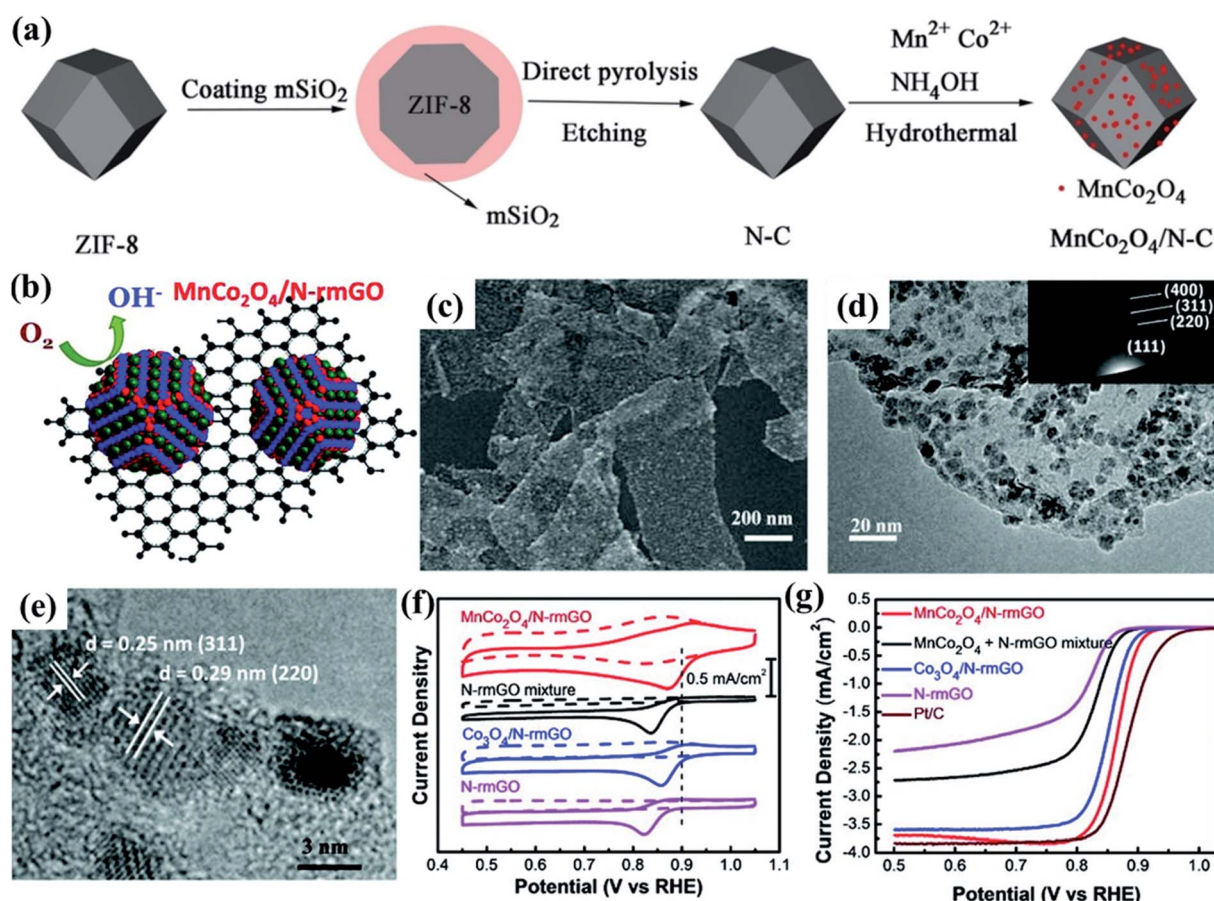


Fig. 9 Schematic illustration of preparation of (a) $\text{MnCo}_2\text{O}_4/\text{N-C}$ nanocomposites. Reproduced with permission from ref. 186. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. Schematic illustration of preparation of (b) the $\text{MnCo}_2\text{O}_4/\text{N-rmGO}$ hybrid. (c) SEM image and (d) TEM image with an inset of the electron diffraction pattern of the $\text{MnCo}_2\text{O}_4/\text{N-rmGO}$ hybrid, respectively. (e) A high-magnification TEM image of the $\text{MnCo}_2\text{O}_4/\text{N-rmGO}$ hybrid. (f) CV curves of the $\text{MnCo}_2\text{O}_4/\text{N-rmGO}$ hybrid, $\text{MnCo}_2\text{O}_4 + \text{N-rmGO}$ mixture, $\text{Co}_3\text{O}_4/\text{N-rmGO}$ hybrid, and N-rmGO on glassy carbon electrodes in O_2 -saturated (solid line) or N_2 -saturated (dashed line) 1 M KOH. The peak position of Pt/C was shown as a dashed line for comparison. (g) Rotating-disk electrode voltammograms of the $\text{MnCo}_2\text{O}_4/\text{N-rmGO}$ hybrid, $\text{MnCo}_2\text{O}_4 + \text{N-rmGO}$ mixture, $\text{Co}_3\text{O}_4/\text{N-rmGO}$ hybrid, N-rmGO, and Pt/C in O_2 -saturated 1 M KOH at a sweep rate of 5 mV s^{-1} at 1600 rpm. Reproduced with permission from ref. 188. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

rmGO sheets, yielding higher activity and stronger durability than the physical mixture of NPs and N-rmGO.¹⁸⁸

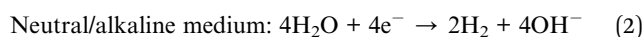
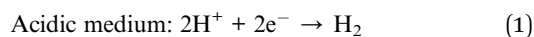
Interestingly, the C–O and C–N bonds in the N-rmGO sheet were strongly perturbed, suggesting the formation of C–O–metal and C–N–metal bonds between N-rmGO and spinel oxide NPs, as confirmed by electrochemical and XANES investigations. As a result, the composite showed a more positive onset (0.95 V *vs.* RHE, Fig. 9f–g) and a greater electron transfer number (~3.9) than the corresponding physical mixture of MnCo₂O₄ NPs and N-rmGO (0.91 V *vs.* RHE and the electron transfer number = ~3.7).¹⁸⁸ Based on the above, it is feasible to mention that the combination of conductivity optimization and active site engineering strategies should benefit the design of advanced ORR electrocatalysts for energy conversion and storage.

4.2. Water-splitting electrocatalysts for energy conversion (OER and HER)

Over the years, the energy demand has increased significantly, and this consumption has intensified year after year, which has led to the depletion of non-renewable energy sources (fossil fuels), as well as an increase in environmental pollution.²⁰⁰ Therefore, the development of new technologies, in which energy is obtained safely, cheaply, and without harming the environment is essential for the preservation of our society.

Among the energy conversion systems, electrochemical water splitting has proved to be very efficient when it comes to obtaining clean and high purity fuels.²⁰¹ In fact, from the electrochemical water splitting it is possible to obtain O₂ and H₂ through OER and HER that occur at the anode and cathode electrodes, respectively.^{2,202}

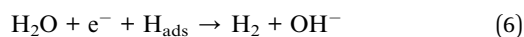
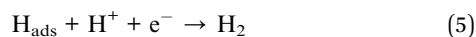
The HER can be expressed depending on electrolyte pH, according to eqn (1) and (2):



In addition, the HER can be divided into two steps called Volmer and Heyrovsky or Tafel pathways, where H_{ads} acts as an intermediate species and plays a crucial role in the mechanism. The first step can proceed in acidic (eqn (3)) and neutral/alkaline solutions (eqn (4)), as indicated by the equations below:



Depending on the coverage ratio of H_{ads} (θ_{H}), the second step can occur through Heyrovsky or Tafel pathways. Whereas the Heyrovsky pathway occurs due to low θ_{H} (eqn (5) in acidic medium and eqn (6) in neutral/alkaline medium), the Tafel pathway occurs in consequence of high θ_{H} , regardless of the pH value (eqn (7)).



However, the obtaining of H₂ is limited by the sluggish reaction kinetics of the OER, because of the four-step electron transfer process (4OH[−] → H₂O + O₂ + 4e[−]) in neutral or alkaline medium.

Currently, catalysts formed by using noble metals, such as RuO₂, IrO₂, and Pt, have been used in electrochemical water splitting in order to overcome the slow reaction kinetics of the OER.²⁰³ However, these catalysts are scarce and expensive, and their use in industry is not feasible. Therefore, noble metal catalysts have been replaced by alternative ones such as layered double hydroxides,^{2,204} oxides,^{205,206} nitrides and sulfides,^{207,208} and spinel structures.^{209,210} Among these catalyst groups, spinel oxides with AB₂O₄ (A and B transition metals) in special MnCo₂O₄ have stood out as promising electrode materials for water splitting due to the ease of preparation, variable valence states and high redox stability in alkaline medium.¹⁹⁴

The main MnCo₂O₄-based catalysts for the OER and HER are shown in Table 5. Most of the studies reported in the literature are related to the electrochemical performance of MnCo₂O₄ concerning the OER, and very few studies were found in the literature using MnCo₂O₄ as an electrocatalyst for the HER, suggesting that there is a vast unexplored field that deserves attention.

Despite advantages mentioned above, the catalytic activity of MnCo₂O₄ is limited by its low electrical conductivity. However, strategies have been explored in order to improve the electrical conductivity such as introduction of hetero-atoms, combining MnCo₂O₄ with conducting materials forming composites, incorporation of oxygen vacancies and nanoparticle size control.

In this sense, Rebekah and co-authors^{211,212} showed that the catalytic activity of MnCo₂O₄ has been improved by the introduction of hetero-atoms (Ni and Zn), as well as by the combination of spinel oxide with rGO. Both Ni and Zn substituted MnCo₂O₄ on the rGO surface were synthesized through a hydrothermal method. The electrochemical behavior of Mn_{1−x}Ni_xCo₂O₄/rGO and Mn_{1−x}Zn_xCo₂O₄/rGO electrodes towards the OER was verified by Linear Sweep Voltammetry (LSV). Better results were achieved for the following compositions, Mn_{0.4}Ni_{0.6}Co₂O₄/rGO²¹¹ (overpotential of 250 mV at 10 mA cm^{−2} and a Tafel slope of 78 mV dec^{−1}) and Mn_{0.8}Zn_{0.2}Co₂O₄/rGO²¹² (overpotential of 320 mV at 10 mA cm^{−2} and a Tafel slope of 80.6 mV dec^{−1}). In summary, good electrochemical performance achieved by Mn_{1−x}Ni_xCo₂O₄/rGO and Mn_{1−x}Zn_xCo₂O₄/rGO electrodes towards the OER can be explained by the faster electron transport due to the more exposed active sites in consequence of the high surface area of rGO and of the reduction of metal ion aggregation owing to stacking between the sheets. In addition, the incorporation of another metallic ion resulted in a material with excellent electrochemical behavior and high conductivity.

The strategy of doping MnCo₂O₄ was also used by Huang *et al.*²¹³ in order to obtain an efficient electrocatalyst for both OER and HER. Indeed, the authors doped MnCo₂O₄ with Ce, being named as Ce–MnCo₂O₄. The OER and HER performances

Table 5 Catalytic activity parameters of recently reported HER/OER MnCo_2O_4 -based electrocatalysts: overpotential at 10 mA cm^{-2} , onset potential, Tafel slope, stability, and pH condition^a

	Catalysts	Substrate	Overpotential at 10 mA cm^{-2} (mV vs. RHE)	Onset potential (V vs. RHE)	Tafel slope (mV dec^{-1})	Stability (h)	pH condition	Ref.
OER catalysts	$\text{MnCo}_2\text{O}_4@\text{CoS}$ NW	NF	280 at 20 mA cm^{-2}	1.51	139.19	10	1.0 M KOH	217
	$\text{MnCo}_2\text{O}_4@\text{CoS}$ NS	NF	270 at 20 mA cm^{-2}	1.50	131.81	10	1.0 M KOH	217
	MCO/NS-MCS	NS-MCS	508	1.738	124	5.5	0.1 M KOH	21
	MnCo_2O_4	—	290	1.52	97	24	1.0 M KOH	193
	$\text{MnCo}_2\text{O}_4@\text{Mn-Co-P}$	Ti	269	1.50	102	100	1.0 M KOH	224
	$\text{Mn}_{1-x}\text{Ni}_x\text{Co}_2\text{O}_4/\text{rGO}$	CGE	250	1.48	78	2.8	1.0 M KOH	211
	$\text{Mn}_{1-x}\text{Zn}_x\text{Co}_2\text{O}_4/\text{rGO}$	GCE	320	1.48	80.6	2.8	1.0 M KOH	212
	YSM-MCO	NF	360	1.59	65.6	80	1.0 M KOH	225
	$\text{MnCo}_2\text{O}_4@\text{Ni}_3\text{S}_2$	NF	200 at 40 mA cm^{-2}	—	43.9	15	1.0 M KOH	226
	$\text{MnCo}_2\text{O}_4/\text{N-rmGO}$	GCE	330	1.56	—	—	1.0 M KOH	188
	$\text{MnCo}_2\text{O}_4\text{-rGO}$	GCE	530	1.56	106.9	—	0.1 M KOH	20
	$\text{Mn}_x\text{Co}_{3-x}\text{O}_4$	NF	327	—	79	25	1.0 M KOH	227
	$\text{MnCo}_2\text{O}_4@\text{Ni}_2\text{P}$	NF	240	—	114	30	1.0 M KOH	221
	$\text{MnCo}_2\text{O}_4@\text{NC}$	GCE	287	1.46	55	20	0.1 M KOH	218
	Ce- MnCo_2O_4	GCE	390	—	125	11.1	1.0 M KOH	213
	CMO/20N-rGO	GCE	450	1.68	80.2	8	0.1 M KOH	187
	Ce- MnCo_2O_4	GCE	389	—	96	12	1.0 M KOH	213
	HER catalysts	$\text{MnCo}_2\text{O}_4@\text{Ni}_2\text{P}$	NF	57	—	89	20	1.0 M KOH
NiFe- $\text{MnCo}_2\text{O}_4/\text{NFF}$		NFF	98	—	80.78	48	1.0 M KOH	19
$\text{MnCo}_2\text{O}_4@\text{Ni}_3\text{S}_2$		NF	110	—	212.15	15	1.0 M KOH	226

^a NW = nanowire; NF = nickel foam; NS = nanosheet; MCO = MnCo_2O_4 ; NS-MCS = nitrogen and sulfur co-doped mesoporous carbon spheres; rGO = reduced graphene oxide; GCE = glassy carbon electrode; YSM = yolk-shell; N-rmGO = N-doped reduced graphene oxide; NC = nitrogen doped carbon; CMO/20N-rGO = $\text{Co}_3\text{O}_4\text{-MnCo}_2\text{O}_4/\text{N}$ -doped reduced graphene oxide with a mass ratio of $\text{NrGO}/(\text{Co} + \text{Mn})$ of ca. 20 wt%; NFF = Ni-Fe foam.

were evaluated by LSV and the material reached an overpotential of 390 and 379 mV, respectively. Those values when compared to MnCo_2O_4 without Ce doping are much superior. In fact, MnCo_2O_4 without Ce presented an overpotential at 10 mA cm^{-2} of 560 and 477 mV, respectively for the OER and HER. The

OER results can be attributed to the introduction of Ce into MnCo_2O_4 that facilitates oxygen transfer through adsorption, dissociation and release of atomic O for the OER, besides the introduction of oxygen vacancies to dissociate water.^{214–216}

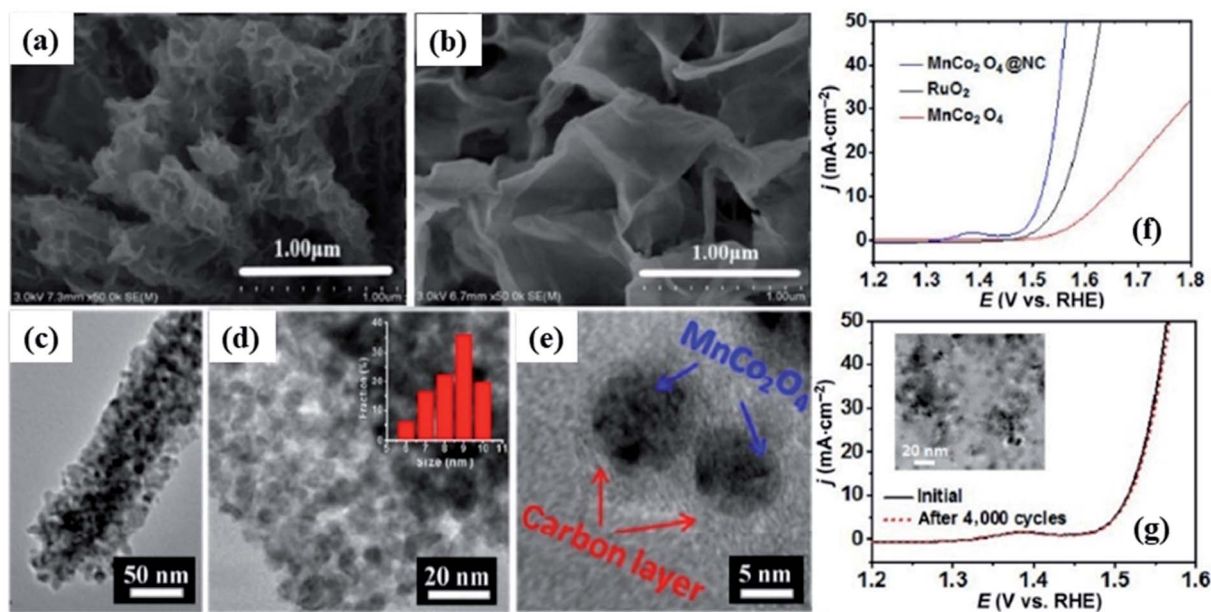


Fig. 10 TEM images of (a) $\text{MnCo}_2\text{O}_4@\text{CoS}$ nanowires and (b) $\text{MnCo}_2\text{O}_4@\text{CoS}$ nanosheets. Reproduced with permission from ref. 217. Copyright © 2019 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved. (c, d) TEM and (e) HRTEM images of $\text{MnCo}_2\text{O}_4@\text{NC}$. (f) LSV curves of $\text{MnCo}_2\text{O}_4@\text{NC}$, RuO_2 and MnCo_2O_4 and (g) LSV initial curve and after 4000 curves for $\text{MnCo}_2\text{O}_4@\text{NC}$. Reproduced with permission from ref. 218. Copyright © 2016, Tsinghua University Press and Springer-Verlag Berlin Heidelberg.

Also, the electrical conductivity of MnCo_2O_4 can be improved through design of hierarchical 3D core@shell structures. Indeed, Du and co-authors²¹⁷ reported the synthesis of two materials based on MnCo_2O_4 @CoS with different morphologies, using a hydrothermal method followed by the electro-deposition technique. As a matter of fact, MnCo_2O_4 @CoS was synthesized in the nanowire and nanosheet shapes, as can be seen in TEM images displayed in Fig. 10a and b, respectively.

The electrocatalytic activity performances of MnCo_2O_4 @CoS with different morphologies towards the OER are very similar, reaching 280 mV and 270 mV at 20 mA cm^{-2} for MnCo_2O_4 @CoS nanowires and MnCo_2O_4 @CoS nanosheets, respectively. Also, the surface areas of the materials were very similar as well. For MnCo_2O_4 @CoS nanowires and MnCo_2O_4 @CoS nanosheets the BET surface areas were 68.46 and $69.38 \text{ m}^2 \text{ g}^{-1}$, respectively. Therefore, the electrochemical results cannot be attributed to the materials' surface area, but it can be related to the synergistic effect between MnCo_2O_4 and CoS, since the poor electrical conductivity of MnCo_2O_4 is compensated by the conductive CoS, and by the abundant oxygen vacancies. In fact, the existence of a large amount of oxygen vacancies can be estimated through XPS studies, where due to the co-existence of Co^{2+} and Co^{3+} ions the molar ratio of $\text{Co}^{2+}/\text{Co}^{3+}$ is a good parameter to evaluate the oxygen vacancies. The molar ratio found for the MnCo_2O_4 @CoS nanowires and MnCo_2O_4 @CoS nanosheets was 0.88 and 0.93, respectively, indicating a large amount of oxygen vacancies.

Over the years, several studies have been reported in the literature where it is demonstrated that the size control of nanoparticles plays a key role in improving the properties of the

materials. Using this strategy, Su *et al.*²¹⁸ encapsulated MnCo_2O_4 nanoparticles using nitrogen-doped carbon (NC), since the NC can not only act as an encapsulating agent controlling the growth of the nanoparticles but also improve the catalytic performance in water splitting.²¹⁹ The MnCo_2O_4 was encapsulated in NC, here denoted as MnCo_2O_4 @NC from a metal-organic complex as a precursor, using a hydrothermal method. The TEM and HRTEM images of the as-prepared material are shown in Fig. 10c–e. It is possible to observe that the MnCo_2O_4 @NC nanowires were made of several well-dispersed nanoparticles with less than 10 nm of average diameter (Fig. 10c). Besides, in Fig. 10e, the HRTEM image of MnCo_2O_4 @NC is displayed, where it is clearly possible to observe that MnCo_2O_4 was encapsulated by NC, forming a core@shell structure. However, the MnCo_2O_4 nanowires without NC presented nanoparticles with an average diameter of 100 nm, demonstrating that the growth of MnCo_2O_4 nanoparticles was limited by the NC.

The results presented above can directly influence the catalytic activity of the material. The MnCo_2O_4 @NC presented an electrochemical performance (overpotential of 287 mV at 10 mV cm^{-2} and Tafel slope of 55 mV dec^{-1}) far superior to that of MnCo_2O_4 nanowires (overpotential of $\sim 420 \text{ mV cm}^{-2}$ and Tafel slope of 101 mV dec^{-1}), Fig. 10f. Also, the MnCo_2O_4 @NC did not show any change in the electrochemical profile after 4000 cycles, as can be seen in Fig. 10g. These results demonstrated that the size control of MnCo_2O_4 nanoparticles (less than 10 nm) using NP, in order to limit the growth of the nanoparticles, provided several active sites are exposed to oxygen adsorption and desorption. Besides, the nanoporous

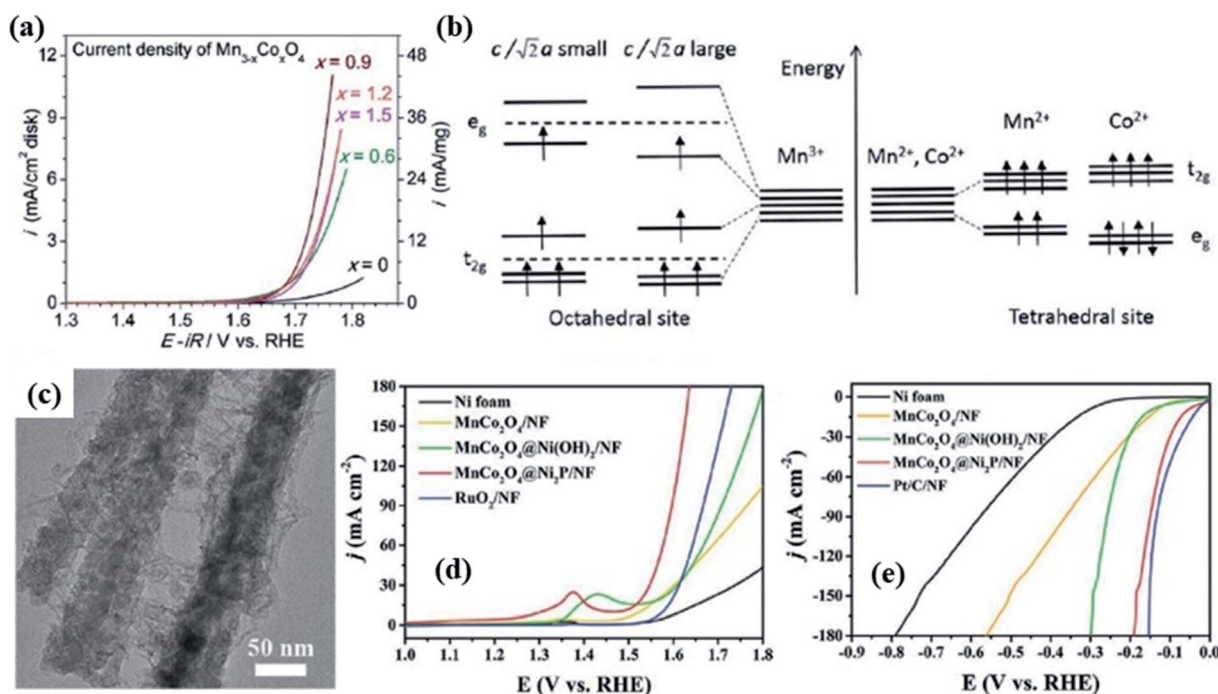


Fig. 11 LSV curves of different samples of $\text{Mn}_{3-x}\text{Co}_x\text{O}_4$ ($0 < x \leq 1.5$) (a) and schematic orbital energy diagram for Mn^{3+} 3d at octahedral sites and Mn^{2+} and Co^{2+} at tetrahedral sites (b). Reproduced with permission from ref. 220. Copyright © Marketplace™, Royal Society of Chemistry. TEM image of MnCo_2O_4 @ Ni_2P (c), LSV curves for the electrocatalytic performance of the OER (d) and HER (e). Reproduced with permission from ref. 221. Copyright © 2020 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

core@shell structure provided easy access of electrolyte ions and improved the electron transfer rate.

Recent studies have pointed out that one of the causes of the low catalytic activity and stability of Co-based compounds for water oxidation is the Jahn–Teller distortion. In this sense, Hirai *et al.*²²⁰ performed a systematic study for tetragonal spinel oxides $\text{Mn}_{3-x}\text{Co}_x\text{O}_4$ ($0 \leq x < 1$ and $1 < x \leq 1.5$) in order to evaluate the relation between the Jahn–Teller distortion and catalytic activity for the OER. They figured out that for $\text{Mn}_{3-x}\text{Co}_x\text{O}_4$ ($0 \leq x < 1$) the catalytic activity was improved with the increase of Co concentration, due to the Jahn–Teller distortion suppression. However, for $\text{Mn}_{3-x}\text{Co}_x\text{O}_4$ ($1 < x \leq 1.5$) the OER activity decreased with Co concentration above 1 up to 1.5, when compared to $\text{Mn}_{3-x}\text{Co}_x\text{O}_4$ ($0 \leq x < 1$), as can be seen through LSV curves in Fig. 11a. Although Mn^{3+} still remains occupying the octahedral sites on the $\text{Mn}_{3-x}\text{Co}_x\text{O}_4$ ($0 \leq x < 1$), when cobalt is added it will occupy the tetrahedral sites, and thus the Jahn–Teller distortion is suppressed, represented by an indicator $c/\sqrt{2a}$ (Fig. 11b) and consequently there is an increase in catalytic activity, due to the strong interaction between the antibonding electron e_g and oxygen species adsorbed (O_2^{2-} and O^{2-}). Nevertheless, when the cobalt concentration is above >1 , the octahedral sites are occupied by a mixture of Mn^{3+} , Co^{3+} , Mn^{4+} , and Co^{2+} ions and then the e_g orbital can be occupied by more than 1 electron or even not be occupied thus decreasing the catalytic activity.

Similarly, Ge *et al.*,²²¹ using an interface engineering strategy to suppress the Jahn–Teller distortion in MnCo_2O_4 , grew Ni_2P nanosheets on the MnCo_2O_4 surface obtaining a bifunctional catalyst for the OER and HER. The $\text{MnCo}_2\text{O}_4@/\text{Ni}_2\text{P}$ was obtained in four steps. The precursor MnCo-LDH was obtained through the hydrothermal method, and then the as-precursor MnCo-LDH was annealed in order to obtain MnCo_2O_4 . A second hydrothermal method was used to deposit $\text{Ni}(\text{OH})_2$ nanosheets on MnCo_2O_4 . After that, the $\text{MnCo}_2\text{O}_4@/\text{Ni}(\text{OH})_2$ was calcined in the presence of NaH_2PO_2 in order to obtain $\text{MnCo}_2\text{O}_4@/\text{Ni}_2\text{P}$. In Fig. 11c the TEM image of $\text{MnCo}_2\text{O}_4@/\text{Ni}_2\text{P}$ is displayed, where it is possible to observe that the MnCo_2O_4 nanoneedles are coated by a large number of Ni_2P nanosheets.

The electrochemical performance of $\text{MnCo}_2\text{O}_4@/\text{Ni}_2\text{P}$ towards the OER and HER was evaluated by LSV, and the curves are shown in Fig. 11d and e. The hierarchical $\text{MnCo}_2\text{O}_4@/\text{Ni}_2\text{P}$ structure exhibited an excellent overpotential for the OER (240 mV at 10 mA cm^{-2}) and a Tafel slope of 114 mV dec^{-1} . Also, the $\text{MnCo}_2\text{O}_4@/\text{Ni}_2\text{P}$ showed an outstanding HER performance with an overpotential of 10 mA cm^{-2} (57 mV) and a Tafel slope of 89 mV dec^{-1} . This HER performance can be explained by the presence of several Ni^0 and Ni^{2+} species, as determined by XPS after phosphorization, once those species can provide energy in order to stabilize the H_{ads} through the weakening of the O–H bond of adsorbed water.²²²

The electronic interactions between MnCo_2O_4 and Ni_2P were clarified through differential charge density. The high charge density is placed on the Ni_2P side, and thus the electrons migrate from Ni_2P to MnCo_2O_4 due to the strong interfacial polarization.²²³ Thus, the strong interaction between $\text{MnCo}_2\text{O}_4@/\text{Ni}_2\text{P}$ reduces the Jahn–Teller distortion and the Ni_2P with

metallic properties increases the electronic conductivity and charge transfer rate of $\text{MnCo}_2\text{O}_4@/\text{Ni}_2\text{P}$.

5. Conclusions and future directions

Lately spinel MnCo_2O_4 -based materials have stood out in the energy conversion and storage technologies, especially due to their low cost, simple preparation and chemical composition versatility obtained through different strategies that enabled the rational design of these materials, thus allowing tuning of their electronic properties. In addition, reducing Co ions in the structure of Co_3O_4 by replacing them with Mn ions has been an excellent strategy to increase the conductivity and improve the electrochemical performance of the electrode materials. In fact, studies have shown that the conductivity of MnCo_2O_4 is greater than that of Co_3O_4 , and its electrochemical performance is superior since Co provides a higher oxidation potential than Mn and Mn brings a higher capacity than Co owing to its efficient electron transport.¹¹⁵ Thus, the recent advances have been summarized in this review and special emphasis was directed to spinel MnCo_2O_4 based materials, which are highly promising for the construction of supercapacitors and batteries, and thus the development of arrangements for water-splitting for energy conversion. It is necessary to highlight that the application of MnCo_2O_4 as a multifunctional material still needs fine control of synthesis conditions, which will impact the phase, morphology, cation distribution, and especially the electrical properties, and it is an important requirement for energy applications.

The construction of supercapacitors using MnCo_2O_4 in the pristine form or as composites based on metal oxides/hydroxides, polymers or carbon-based composites or other materials was described as an important strategy to increase the capacitance and rate capability of hybrid devices, resulting in supercapacitors with higher energy and power density.

Additionally, LIBs, SIBs and metal– O_2 batteries are also covered. In order to improve the electrochemical performance in LIBs, in addition to developing composites of MnCo_2O_4 with other materials, morphological modifications and synthesis methods have been the focus of researchers, particularly on the preparation of porous materials (mesoporous, hollow, yolk-shell, shell-in-shell, and yolk-in-double-shell spheres). Mesoporous transition metal-doped MnCo_2O_4 has also been reported for application in SIBs, while heteroatoms doped-carbon materials were mixed with MnCo_2O_4 due to intrinsic advantages as ORR catalysts, such as high surface area and electrochemical stability in metal– O_2 batteries. The results obtained with MnCo_2O_4 for the construction of supercapacitors, metal-ion batteries, and metal–air batteries were tabulated.

Conversely, MnCo_2O_4 based materials showed great potential as electrocatalysts in energy storage devices. For instance, conductivity optimization by the formation of composites with conducting carbon materials has been the main strategy for preparing excellent electrocatalysts for the ORR (or bifunctional electrocatalysts for the OER/ORR). However, porous spinels with tunable size, shape, chemical composition and crystalline structure were also reported *via* a facile precursor pyrolysis method.

MnCo₂O₄ was also recently used as an electrocatalyst for energy conversion, mainly in water splitting. Most of the studies reported in the literature are related to the electrochemical performance of MnCo₂O₄ concerning the OER, and very few studies were found in the literature using MnCo₂O₄ as an electrocatalyst for the HER, suggesting that there is a vast unexplored field that deserves attention. Thereunto, strategies have been explored in order to improve the electrical conductivity and electrocatalytic activity, such as introduction of hetero-atoms (or doping), combination with conducting materials forming composites, incorporation of oxygen vacancies and nanoparticle size control.

As demonstrated in this article, the utilization of spinel MnCo₂O₄-based materials for energy storage and conversion is a promising new concept in energy technologies. It is also important to highlight that future research should continue to enrich spinel MnCo₂O₄-based materials, focusing attention on the electrochemical performance and reasonable architectural design of those materials for practical application in energy technologies and expanding the fields of application. In fact, it is possible to visualize a field still unexplored and of great potential for application, for instance, the rational design of different composite materials composed of MnCo₂O₄ and/or heterojunctions containing the recent advanced 2D materials (such as MXene, transition metal chalcogenides, black phosphorus, etc.), aiming at future applications of these supercapacitor/battery materials for flexible/wearable devices, self-charged energy storage devices, and microsupercapacitors. The future applications of flexible/wearable energy devices depend on suitable flexible substrates that can stably and efficiently incorporate MnCo₂O₄ or its composites. In this direction, novel current collectors have been investigated and carbon cloth has shown promising results due to its excellent flexibility and conductivity. Additionally, different synthesis strategies urge investigation, and in this sense, electrochemical growth on flexible conductive substrates is promising (without binders and using a simplified rotocol). Considering large-scale and reproducible production, additive manufacturing (or three-dimensional printing) protocols offer great promise in this area.

Moreover, bifunctional and multifunctional catalysts represent promising directions,¹⁵ especially for electrocatalysts for water splitting (HER/OER) and metal–air batteries (ORR/OER). Other applications, such as the use of MnCo₂O₄ catalysts to convert greenhouse gases (CO₂) and toxic gas (CO) into chemical fuels, are also feasible. From this perspective, MnCo₂O₄-based materials have a key role in the way to a more sustainable society and industrial applications.

Conflicts of interest

The authors declare that there is no conflict of interest.

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