## 1

# Fundamentals of Nanomaterials in Energy Systems

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# 1.1 Introduction

Nanomaterials, such as nanoparticles, nanotubes, nanowires, and quantum dots, are of interest in various application areas of technology. They are revolutionizing energy systems and improving the efficiency of energy conversion, storage, and utilization processes due to their properties, such as surface with excellent electron transport capacity, physicochemical properties, mechanical strength, and unique dimensions, which offer advantages and advances in new technologies [1–5]. These properties of nanomaterials have become interesting for supercapacitors, fuel cells, solid-state batteries, photocatalysis, light-emitting diodes, hydrogen storage systems, etc. [1, 2, 6–10].

However, the integration of nanomaterials into energy systems is associated with challenges, such as sustainability and renewable energy, improving energy storage, reducing environmental impact, and conditioning materials with specific system properties [1, 11]. For example, suppose that the size of nanomaterials in semiconductors is reduced (Figure 1.1). In this case, the band gap increases due to the quantum confinement effect, and the optical properties such as absorption, emission, and excitation can be adjusted [12–14]. In solar energy applications, nanomaterials can significantly improve the light absorption and conversion efficiency of photovoltaic cells. In battery technology, these materials achieve higher energy densities, fast charging times, and a long service life [10, 15, 16]. For the development of fuel cells, supercapacitors, and hydrogen storage, nanomaterials facilitate efficient electrochemical reactions in the storage of large amounts of energy in a compact form, making them indispensable in the search for next-generation energy solutions [6, 12, 17–21]. Compared to carbon-based nanomaterials, which have minimal surface defects, this composition is critical as an alternative to stainless



**Figure 1.1** Schematic overview of the applications of nanomaterials in various fields.

steel or iron for mechanical strength and stability. Further studies are required to confirm its feasibility as a replacement.

Understanding the fundamentals of nanomaterials and their applications in energy systems is critical for research groups seeking to innovate and improve energy technologies [4, 13, 22, 23]. This introduction provides an overview of the progress and potential future directions in the field of nanomaterials for energy storage and conversion of energy systems.

This chapter highlights future research opportunities and proposes solutions to bridge the gap between fundamental research and real-world applications in next-generation energy technologies.

### 1.1.1 Nanomaterials in Battery Systems

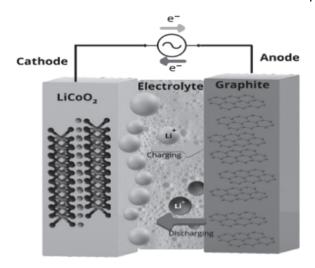
Nanomaterials have significantly improved energy conversion and storage in battery systems, especially in lithium-ion, Li-S, metal-air, and solid-state batteries. They improve electrochemical reaction kinetics; reduce ion diffusion pathways; and improve stability, surface area, cycle life, and miniaturization. The main components of battery systems in which energy conversion takes place are the cathode, the anode, the separator, and the electrolyte. Together they ensure the cell voltage (E), the energy and potential density, the stability, and the service life.

Lithium-ion batteries (LIBs), as shown in Figure 1.2, typically use graphite for the anode and  $LiCoO_2$  for the cathode, resulting in an energy density of around 150 Wh kg<sup>-1</sup>. This energy density is achieved by the movement of lithium ions through the internal passageway and electrons through the external circuit, which eventually return to the positive electrode. The following equation illustrates the ideal electrochemical reactions that take place during the charge/discharge process, with the cathode reaction represented by given Eqs. (1.1) and (1.2) showing what happens in the anode [24].

$$LiCoO_2 \leftrightarrow xLi^+ + xe^- + Li_{1-x}CoO_2$$
 (1.1)

$$6C + xLi^{+} + xe^{-} \leftrightarrow Li_{x}C_{6} \tag{1.2}$$

Figure 1.2 Schematic of a lithium-ion battery (LIB).



Research into nanomaterials in LIBs has significantly improved their efficiency in meeting new energy needs, e.g. in electric vehicles and trains, and even in meeting lower energy needs, e.g. in biomedical devices. For example, Si-based nanomaterials have attracted interest as anode electrode materials due to their theoretical capacity of 4200 mAh  $g^{-1}$  compared to that of graphite (372 mAh  $g^{-1}$ ).

### i) Nanomaterials for the Anode

Conventionally, graphite is the most widely used material in LIBs, although this material tends to degrade, limiting its useful life. Carbon-based nanomaterials, such as carbon nanotubes (CNTs), carbon nanofibers, porous carbon, and graphene, have been investigated to reduce this drawback. In addition, other nanostructured materials that are not carbon-based have been reported. These include Ti/TiO<sub>2</sub>-based materials, Si-based materials, spinel Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>, germanium, and metal oxides as iron and cobalt, which have the potential to improve the performance of the anode [25].

### ii) Nanomaterials for the Cathode

Lithium nickel manganese cobalt oxide (NMC) and lithium manganese oxide (LMO) usually have a long lifetime with about 500 charge/discharge cycles. NMC offers specific capacities of 150-220 Wh kg<sup>-1</sup>, while LMO delivers 100-150 Wh kg<sup>-1</sup>. Other Li-based nanomaterials have been reported, such as LiCoO<sub>2</sub>, LiMn<sub>2</sub>O<sub>4</sub>, LiNiO<sub>2</sub>, LiFePO<sub>4</sub>, LiMnPO<sub>4</sub>, LiFeSO<sub>4</sub>F, LiCoNiMnO<sub>2</sub>, LiNiCoMnO<sub>2</sub>O, and lithium-nickel-cobalt-manganese (Li-Ni-Co-Mn), in which there are several monoanionic and polyanionic compounds whose chemistry is favored for their high-energy storage capacity [24].

### iii) Separator

The separator is usually a porous material that separates the anode and cathode to prevent short circuits, allowing the battery to charge/discharge. Polymers such as polyethylene and polypropylene are usually used, but they have limitations such as low stability in mechanical strength, low melting points, and lower chemical resistance, which reduce the efficiency of the battery's overall performance. Nanomaterials such as SiO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub> are alternatives to these inconvenient materials, which mainly bring advantages such as high porosity and chemical and mechanical resistance [25].

### iv) Electrolyte

Electrolytes enable the movement of positive lithium ions between the electrodes in LIBs. There are two types of electrolyte materials: solid polymer electrolytes (SPEs) and liquid electrolytes (LEs). An SPE consists of a solid polymer matrix infused with lithium salts. Ceramic nanopowders investigated in this context include Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, and Li<sub>14</sub>Al<sub>04</sub>Ti<sub>16</sub>(PO<sub>4</sub>)<sub>3</sub>, which can be incorporated into polyethylene-based electrolytes to improve stability. In addition, SiO<sub>2</sub> (MA-SiO<sub>2</sub>)-nanostructured materials functionalized with methacrylate are used for electrolytes in LIBs. In recent years, solid-state and gel electrolytes have been investigated and nanomaterials or nanostructured additives have been integrated to improve ion transport in batteries [25].

## v) Lithium-Sulfur Batteries (LSBs)

Another type of battery used in energy systems are lithium-sulfur batteries (LSBs), which have a theoretical capacity of 1675 mA hg<sup>-1</sup> and a gravimetric and volumetric energy density of 2500 Wh kg<sup>-1</sup> and 2800 W h L<sup>-1</sup>, respectively, compared to LIBs. The components of this type of battery are the same as those of LIBs: cathode, anode, separator, and electrolyte. Nanomaterials such as LiCoO<sub>2</sub>, LiFePO<sub>4</sub>, LiMnO<sub>2</sub>, tetratitanium heptoxide (Ti<sub>4</sub>O<sub>7</sub>), and Ti-O<sub>2</sub>-TiN heterostructure have been described for use as cathodes for LSBs, with a discharge capacity of 704 mAh g<sup>-1</sup> at the 2000th cycle. In addition, perovskite-based materials such as  $La_{0.6}Sr_{0.4}CoO_3$ - $\delta$  and  $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3 - \delta$  can immobilize polysulfides through chemical bonding between lithium and oxygen or sulphidic and sulfur, resulting in improved performance [26].

CNTs were used for the anode. Graphene, a 2D nanomaterial, forms nanoparticles together with 3D hybrid nanomaterials and a metal oxide or sulfide clusters, which are added to the sulfur-carbon nanostructures to achieve high performance. Examples are CeO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, MgO, and CaO.

### vi) Zinc-Air Batteries

Zinc-air batteries (ZABs) use Zn as the reaction electrode due to their cost advantage, reversibility, and a promising theoretical specific energy of 1350 Wh kg<sup>-1</sup>. However, their practical specific energy is only about 200 Wh kg<sup>-1</sup>. Their disadvantage is their limited performance and application. This type of battery is divided into alkaline and non-alkaline systems. In the mechanism of ZABs shown in Figure 1.3, zinc and oxygen react to complete the redox process and generate electricity, using Zn at the anode and air at the cathode in the presence of an electrolyte [27, 28]. In charging, the overall reaction involves ZnO to generate Zn and O2, whereas in discharging the process is reversible and cyclic.

Carbon nanomaterials such as CNTs and CNFs were used as substrates and even mixed with nanomaterials. Among the nanomaterials for Zn electrodes,

**Figure 1.3** The mechanism of the zinc-air batteries (ZABs).

### Charge

Cathode:  $ZnO + H_2O + 2OH^- \rightarrow Zn(OH)_4^{2-}$  $Zn(OH)_4^{2-} + 2e^- \rightarrow Zn + 4OH^-$ Anode:  $2OH^{-} \rightarrow \frac{1}{2}O2 + H_{2}O + 2e^{-}$ Overall reaction: 2ZnO → 2Zn + O<sub>2</sub>

### Discharge

Negative electrode:  $Zn + 4OH^- \rightarrow Zn(OH)_4^{2-} + 2e^ Zn(OH)_4^{2-} \rightarrow ZnO + H_2O + 2OH^-$ Positive electrode:  $\frac{1}{2}$  O2 + H<sub>2</sub>O + 2e<sup>-</sup>  $\rightarrow$  2OH<sup>-</sup>

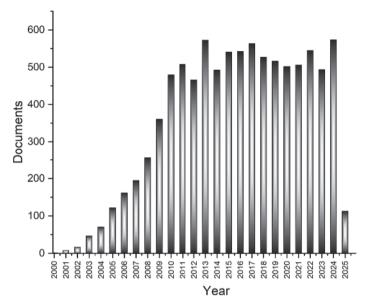
Overall reaction: 2Zn + O₂ → 2ZnO

the use of ZnZnO/C, Zn/CNT, ZnZu/Zn, Zn-ZnO@/C, ZnO/C, Zn@ZSO, C/Zn, Zn/ZnO-N-C, Ti<sub>2</sub>C<sub>2</sub>Tx@Zn, and Zn/CNT has been reported, and it should be noted that core-shell materials and bimetallic materials have been reported. While the electrolyte is an important component of this type of battery, they have been improved by the addition of nanomaterials to increase their efficiency in ion transport. 3D Nanoporous composites, Zn nanoarrays, nanoshells/nanoparticles, Cu nanowire Zn-Si-O nanosheets, Zn nanosheets, Zn-N-C microsheets, and ZnO nanorod-GO have been reported to show improvements in efficiency, energy, and cycling [29].

#### Nanomaterials in Fuel Cells 1.1.2

A fuel cell (FC) is a type of electrochemical system for generating electricity through chemical reactions using a constant flow of fuel and oxidizing agent. The components of an FC are the anode, the cathode, the electrolyte, the fuel, the oxidizing agent, and the membrane (except for microfluidic FC membranes) [30]. There are different types of fuels such as proton exchange membrane fuel cells (PEMFCs), phosphoric acid fuel cells (PAFCs), molten carbonate fuel cells (MCFCs), solid oxide fuel cells (SOFCs), alkaline fuel cells (AFCs), and microbial fuel cells (MFCs). It can even include biofuel cells and microfluidic fuel cells. Depending on the type of FC, they produce different power outputs at different operating temperatures; AFCs can operate at room temperature and are reported to have a power output of 100 kW, followed by PEMFCs between 100 and 250 kW, MCFCs at 1000 kW, PAFCs between 1000 and 2000 kW, and SOFCs up to 3000 kW but at a temperature of up to 1000°C [31].

The diverse and continuous research of FCs is mainly due to their applications and prospects, such as fuel storage, green applications, automotive, aerospace, stationary power, portable power, small electronics, and military applications, which is why they continue to be investigated [31]. A search in Scopus using the keywords nanomaterials and fuel cell shows an increase in publications since 2007 to a maximum of 600 articles per year. In this context, nanomaterials have played an important role in improving performance, lifetime, output power, and current, opening up the possibility of commercializing this device (Figure 1.4).



**Figure 1.4** Technological advances in nanomaterials for fuel cells. Source: Adapted from Scopus®.

# 1.1.3 Nanocatalysts for Fuel Oxidation

In FCs, the oxidation of the fuel, which can be mainly methanol, ethanol, or hydrogen, takes place at the anode, where electrons are generated that travel in an external circuit, while ions in the electrolyte migrate to the cathode. The first nanomaterials used came from noble metals such as Au, Ag, Pd, and Pt as well as from bimetals in the form of alloys, layers, and core–shells such as Au@Pd, Au@Pt, Pt@Pd, and Pd@Pt, but also from other combinations with metals that help to reduce the amount of noble metal, such as Pt–Co–ZrO<sub>2</sub>/MWCNTs, Pt–Fe in a nitrogen-doped carbon carrier, and Pt–Ga nanowires made of an ultra-thin alloy. It is worth mentioning that several of these nanocatalysts are supported on carbonaceous nanoparticles such as MWCNTs, rGO, GO, nanofibers, or some non-carbonaceous ones such as ZrO<sub>2</sub>, TiO<sub>2</sub>, indium oxides, alumina, silica and tungsten oxide, ceria, and conducting polymer nanomaterials [32].

While, in the cathode, for the oxygen reduction reaction (ORR), the chemical reaction in which oxygen is reduced to water, Pt is usually preferred or mixed with other metals to reduce the amount used but with similar efficiencies such as Pt–Fe, Pt–Cr and Pt–Cr–Co, FeNCS, Ni/C, FeNi–NC, AgAg<sub>2</sub>WO<sub>4</sub>, AgCoCu-rGO, Fe–N–C, Zn–N–C, FeN<sub>4</sub>–O-NCR, Cu/CuONC-900, Mn, Ni/NCNTs, Bi<sub>2</sub>SiO<sub>5</sub>NG, N-doped porous CNFs, N, F co-doped CNFs, Fe–N, No–N–CNFs, FeNi–N, NiCo–N–NFs, NiCo, ZnCo, LaCoO<sub>3</sub>, and CaMnO<sub>3</sub> [33].

In the FCs using proton exchange membranes (PEM) (Figure 1.5), whose function is ion transport, which can be protonic or anionic, Nafion\* was mainly used as the perfluorosulfonate resin. However, other membranes with similar properties were also investigated, such as poly(ether ether ketone) (PEEK),

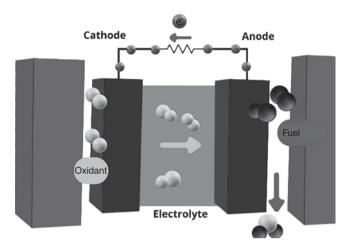


Figure 1.5 FCs that use PEM membranes.

[4, 13, 22-24] polybenzimidazole (PBI), [29-32] polystyrene sulfonate (PSS), [33, 34] polyvinylidene fluoride (PVDF) and its copolymers, and 41–44 polysulfone (PSU), which has its advantages and disadvantages, such as solubility, low ionic conductivity, low mechanical, or temperature stability, which is why its composition with nanomaterials as silica titania MOFs, MoS2 two-dimensional nanomaterials, graphene oxide, boron nitride, zeolite, ZrP, and silica/bentonite was investigated to improve proton conductivity, membrane stability, permeability, and terminal and mechanical stability [34-36].

#### Nanomaterials for Photovoltaic Cells 1.1.4

Solar or photovoltaic (PV) cells are technological energy systems that convert solar energy into sustainable and environmentally friendly electrical energy. This promising energy system is currently used for powering homes, water heating, solar power plants, solar-powered transportation, space applications, portable electronics, and charging stations. The amount of energy produced can be calculated by taking into account the theoretical energy efficiency of the cell, which can produce in a given time given a percentage of its stated output. This means that a cell with an energy efficiency of 300 W for five hours and 80% of its power could produce 1200 Wh or 1.2 kW day<sup>-1</sup>, which could theoretically cover the energy consumption of an average household. On the other hand, it has some disadvantages, such as intermittent energy, the installation is expensive, the technology has not yet reached a high efficiency to meet the daily demand in medium/large cities, and constant maintenance or replacement of the cells is necessary [37].

The power conversion efficiency (Z) of these devices is given by Eq. (1.3). Pinc is the incident solar power, V<sub>OC</sub> is the open circuit voltage, J<sub>SC</sub> is the short-circuit current density, and FF is the fill factor. J<sub>SC</sub> is the current density at zero bias voltage and  $V_{\text{OC}}$  is the maximum voltage that a solar cell can generate. This conversion efficiency can vary depending on the material used and physical aspects such as light irradiation, light absorption, separation of electrons and holes, transport of charge carriers generated by light to the electrodes, and energy dissipation in the circuit [38].

$$n = \frac{V_{\rm OC}J_{\rm SC}FF}{P_{\rm inc}} \tag{1.3}$$

The development of PV cells includes the first generation of silicon solar cells, which were characterized by a relatively high efficiency but were associated with high manufacturing and installation costs. The second generation of thin-film solar cells used amorphous silicon, polycrystalline silicon, CdTe, and Cu-Ir-Ga-Se; these technologies were less expensive and increased production throughput. The third generation of solar technologies aims to reduce costs while maintaining high solar energy conversion efficiencies. These technologies include dye-sensitized solar cells (DSSCs), organic photovoltaics, inorganic photovoltaics in the solution process, and colloidal quantum dot solar cells. Currently, solar cells made from crystalline, polycrystalline, and amorphous silicon account for more than 90% of global production [38].

In this sense, nanomaterials have emerged as a new alternative to achieve higher efficiency in the conversion of solar energy into electrical energy, reduce costs, find more affordable materials, extend useful life, increase energy efficiency in portable devices, and miniaturize them. In addition to Si nanoparticles and Si-based materials, quantum dots (QDs) and quantum rods (QRs), nanomaterials that have the property of being semiconductors and utilize the absorption of light across the spectrum, depending on the choice of a semiconductor material due to its intrinsic bandgap tuning properties, have also been presented. Lead sulfide (PbS) and group IV-VI QDs have already been documented, each absorbing in different spectral regions. Similarly, the quantum confinement effect allows the absolute positions of quantized energy levels to be adjusted. For example, modifications to cadmium selenide (CdSe) and cadmium telluride (CdTe) QDs have shown the potential to manipulate the charge separation at interfaces. In addition, consideration of the plasmonic properties of nanostructures can improve light concentration and energy efficiency. Various materials, including Si, InP/InGaAsP, and GaAs, and group IVB transition metal nitrides (TMNs), such as titanium nitride (TiN), zirconium nitride (ZrN), and hafnium nitride (HfN), have already been described [39].

One strategy to increase the performance of PV cells is to use inorganic semiconductor/polymer nanocomposites with hole-conducting polymers and semiconductor quantum materials such as CdSe, PbS, and PbSe QDs or QRs. This approach combines the advantages of both materials: low-cost, easy processing in solution, lightweight, flexible substrates, and high electron mobility, which is influenced by size, optical bandgap, and plasmonic properties. Some quantum-confined nanocrystals such as PbS, PbSe, PbTe, CdSe, InAs, InP, and Si-modified materials exhibit multiple exciton generation with a quantum yield of over 100%, improving the short-circuit current of solar cells [40].

#### 1.1.5 Nanomaterials for the Application of Capacitors

Electrochemical capacitors enable energy storage by ion adsorption (electrochemical double-layer capacitors) or in the non-Faradaic part of the charge/discharge at the interface between a material and an electrolyte (pseudocapacitors). We can also mention ultracapacitors or supercapacitors, which can be charged/discharged quickly and have a lower energy density (5 Wh  $kg^{-1}$ ) but a high power (10 kW  $kg^{-1}$ ). Hybrid capacitors are a combination of a capacitor electrode and a battery electrode, combining both the advantages and disadvantages of both systems. They have gained attention due to their applications, especially in transportation, such as hybrid electric vehicles, subways, and streetcars [41].

Electrochemical double-layer capacitors (EDLCs) store energy by electrostatic charging using the reversible absorption of electrolyte ions within the electroactive material; charge separation occurs upon polarization at the electrode-electrolyte interface and is described by Eq. (1.4).

$$C/A = \frac{\varepsilon_r \varepsilon_0}{d} \tag{1.4}$$

where  $\varepsilon_r$  is the electrolytic dielectric constant,  $\varepsilon_0$  is the dielectric constant, d is the double layer thickness, and A is the electrode surface area. The capacitance model of Goury-Chapman-Stern-Geary, in which the stored energy (E) is proportional to the square of the voltage, is also accepted, as shown in Eq. (1.5):

$$E = \frac{1}{2} \text{CV}^2 \tag{1.5}$$

Capacitance is investigated using electrochemical techniques such as cyclic voltammetry (CV), galvanostatic charge/discharge, and electrochemical impedance spectroscopy. These methods enable the calculation of the specific capacitance  $(C_{sp})$ . The key variables include the charge (Q), electrode mass (m), potential window ( $\Delta V$ ), discharge current (I), and discharge time ( $\Delta t$ ).

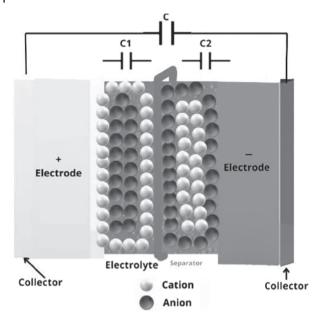
$$C_{sp} = \frac{Q}{m\Delta V}$$
 by cyclic voltammetry (1.6)

$$C_{sp} = \frac{I\Delta t}{m\Delta V}$$
 by galvanostatic charge/discharge (1.7)

A  $C_{sp}$  shows a more efficient capacitor for storing energy and the energy distribution with the charging/discharging times, Figure 1.6 [42]. As can be observed in both systems, the efficiency of the capacitance is directly related to the type of material used, making nanomaterials a widely used resource due to their versatility, large surface area, and charge storage. These nanomaterials can be made from carbon, metal oxides, and hybrids with 0, 1, 2, and 3 dimensions [43].

### Carbon Nanomaterials

CNTs are used as supports, hydrogen storage devices, batteries, sensors/biosensors, fuel cells, semiconductors, and supercapacitors. Due to their high porosity, larger surface area, and higher charge transport capacity, they can be doped with hydrogen atoms that improve their capacitive properties. This type of material has been



**Figure 1.6** Schematic of an electrochemical double-layer capacitor.

reported to have a higher capacitance, close to the estimated theoretical capacitance  $(71-178 \, \text{Fg}^{-1})$  [44].

Graphene foam is a two-dimensional material with  $\rm sp^2$  hybridization of polycyclic aromatic hydrocarbons. It has demonstrated an energy density of 26 Wh kg<sup>-1</sup> using an organic electrolyte (1 M LiPF<sub>6</sub>). Other features include a high theoretical specific surface area of 2630 m<sup>2</sup> g<sup>-1</sup> and the ability to facilitate electron transfer along its surface, with a very low charge transfer resistance [44].

# 1.1.6.1 Activated Carbon

Activated carbon is characterized by a large surface area, favorable electrical properties, low cost, and capacitance properties compared to those of graphene and CNTs [44].

Mesoporous carbon (MC) is ideal for supercapacitor electrodes due to its large specific surface area with different pore sizes. In the synthesis of ordered mesoporous carbon, a mixture containing P-doped MC, which has a better porous structure than undoped MC, is pyrolyzed. This structure has a specific surface area of 403.5 m $^2$  g $^{-1}$ , a pore volume of 0.545 m $^3$  g $^{-1}$ , and an average pore size of 4.64 nm. P-doped MC has a higher specific capacitance of 288 F g $^{-1}$  and a robust cycle stability of 97.6% [44].

## 1.1.7 Metal Oxides/hydroxides

The capacitance values of metal oxides/hydroxides are significantly lower than those of carbon nanomaterials, as their specific pseudocapacitance exceeds that of carbon materials. In addition, they are very versatile and can be used in different types of

structures. They support corrosion, are friendly to the supporting electrolyte, and improve their specific capacities [42].

Ruthenium oxide (RuO<sub>2</sub>) is well studied because of its high pseudocapacitance, estimated at 1450 Fg<sup>-1</sup> and 1360 Fg<sup>-1</sup>. Various nanostructures such as nanotubes, nanorods, nanoflowers, and nanosheets have been investigated. Mesoporous RuO<sub>2</sub> with a high surface area of 140 m<sup>2</sup> g<sup>-1</sup> has a capacity of 202 Fg<sup>-1</sup> compared to 146 Fg<sup>-1</sup> with a lower surface area of 39 m<sup>2</sup> g<sup>-1</sup>, emphasizing the importance of surface area.

Another much-studied metal oxide is manganese oxide (MnO<sub>2</sub>), which is inexpensive and less toxic than RuO2. MnO2 has a high theoretical specific capacity of 1370 Fg<sup>-1</sup>. Nickel-based compounds such as NiO/Ni(OH), have also been investigated in various structures including porous films, hollow nanospheres, nanoribbon nanoplatelets, nanorod arrays, nanowires, nanoflakes, nanosheets, nanowhiskers, flower-like microspheres, 3D dendrites, and nanoflowers due to their diverse surfaces for Faradaic reactions and high specific capacitance.

Other metal oxides with pseudocapacitance properties have also been reported, including Co<sub>3</sub>O<sub>4</sub>/Co(OH)<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>/Fe<sub>3</sub>O<sub>4</sub>, Cu<sub>2</sub>O/CuO, V<sub>2</sub>O<sub>5</sub>, SnO<sub>2</sub>, Bi<sub>2</sub>O<sub>3</sub>, and titanium oxide-based nanowires. However, individual metal oxides are often subject to various limitations and generally have a lower energy storage capacity. To solve these problems, researchers have explored different types of core-shell and bimetallic metal oxides. Examples include various spinel metal oxides such as MnCo<sub>2</sub>O<sub>4</sub>, CoMn<sub>2</sub>O<sub>4</sub>, MnNi<sub>2</sub>O<sub>4</sub>, NiCo<sub>2</sub>O<sub>4</sub>, NiMn<sub>2</sub>O<sub>4</sub>, and ZnCo<sub>2</sub>O<sub>4</sub>. For example, porous nanowires made of MnCo2O4 have been reported to have a surface area of 106.6 m<sup>2</sup>g<sup>-1</sup> and a high specific capacitance of 2108 Fg<sup>-1</sup> [42].

#### 1.1.8 **Conductive Polymers**

Conductive polymers (CPs) provide pseudocapacitance through fast reversible redox reactions of p-conjugated polymer chains but have limited nanostructural morphology and lower capacitive performance than metal oxides. Their advantages lie in their flexibility, higher conductivity, and ability to form thin films. Examples of these CPs are polyaniline, polypyrrole, and polythiophene, whose pseudocapacitance performance largely depends on phase crystallinity, surface area, morphology, conductivity, and mass loading over the electrode substrates [44].

Hybrid materials that combine metal oxides and conductive polymers have problems with cyclicity due to volume changes. To solve this problem, nanostructural composites with stable carbon materials such as carbon nanotubes, graphene, carbon dots, and activated carbon are preferred. For example, CuO@MnO2/N-MWCNT composite electrodes achieve a specific capacitance of 184 F g<sup>-1</sup> at 0.5 A g<sup>-1</sup>. Similarly, SiC@PANI electrodes offer a specific capacitance of 352 mF cm<sup>-2</sup> at 1 mA cm<sup>-2</sup>, outperforming SiC or PANI (polyaniline) alone. In addition, 20 wt% PANI/MoOx nanowires exhibit a specific capacitance of 450 Fg<sup>-1</sup> [45].

Hybrid supercapacitors showed improved electrochemical performance when two different electrodes with different materials were used, such as ZnSnO<sub>3</sub>@In<sub>2</sub>O<sub>3</sub> core-shell microfibers as well as Fe<sub>2</sub>O<sub>3-x</sub>@rGO/MnO<sub>2</sub>/rGO, CS@ZnO core-shell NCs, and RGO/MnOx@HCNs exhibit a high specific surface area ranging from 493 to 668 m<sup>2</sup> as significant MnO, which has a specific capacitance of 355 Fg<sup>-1</sup> at a current density of  $1 \,\mathrm{Ag^{-1}}$  and  $270 \,\mathrm{Fg^{-1}}$  at  $1.0 \,\mathrm{Ag^{-1}}$  in a two-electrode system using 6 M KOH as the electrolyte medium. These technologies improve stability and cycle life, and, in some cases, lead to a higher capacity by reducing the pseudocapacitance [45].

#### 1.2 **Conclusions**

In summary, nanomaterials have fundamentally advanced energy systems by improving the performance, stability, and longevity of battery components. Their diverse applications in anodes, cathodes, separators, and electrolytes underline their central role in the development of high-performance energy storage solutions. Continued research and development of nanomaterials promises further improvements in the efficiency and performance of future energy systems.

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