Ceramic-Based Hybrid Supercapacitors

Subjects: Nanoscience & Nanotechnology | Chemistry, Applied | Electrochemistry

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Supercapacitors (SCs) have attracted considerable attention among various energy storage devices due to their high specific capacity, high power density, long cycle life, economic efficiency, environmental friendliness, high safety, and fast charge/discharge rates. SCs are devices that can store large amounts of electrical energy and release it quickly, making them ideal for use in a wide range of applications. They are often used in conjunction with batteries to provide a power boost when needed and can also be used as a standalone power source. They can be used in various potential applications, such as portable equipment, smart electronic systems, electric vehicles, and grid energy storage systems.

carbon-based materials metal oxides conductive polymers

1. Introduction

In recent years, the world has experienced an increase in development, leading to energy shortages and global warming. These problems have underscored the need for supercapacitors as green energy storage devices. Supercapacitors can store large amounts of energy and deliver excellent power, making them ideal for various applications. Supercapacitors are an increasingly attractive option in the race to develop new and improved energy storage technologies due to their high-power density and long cycle life. As the supercapacitor market grows, so does the need for improved fabrication processes and electrode materials. Supercapacitors have several advantages over other energy storage devices. They can charge and discharge quickly, making them well-suited for various applications. In addition, supercapacitors are environmentally friendly and have a long lifetime. Supercapacitors are expected to grow in the coming years as the world looks for ways to address energy shortages and global warming.

Identifying clean and renewable new energy sources and developing efficient energy storage technologies and devices for low-carbon and sustainable economic development have become important [1][2][3][4]. Common electrochemical energy storage and conversion systems include batteries, capacitors, and supercapacitors [5]. The three energy storage systems complement each other in practical applications and meet different needs in different situations. Although the three systems have different energy storage and conversion mechanisms, they are all based on similar electrochemical thermodynamics and kinetics, i.e., the process of supplying energy occurs at the phase boundary of the electrode/electrolyte interface with independent electron and ion transport [6]. Recent advances in smart electronic devices have spurred a corresponding increase in the use of supercapacitors.

A supercapacitor is a promising energy storage device between a traditional physical capacitor and a battery. Based on the differences in energy storage models and structures, supercapacitors are generally divided into three categories: electrochemical double-layer capacitors (EDLCs), redox electrochemical capacitors (pseudocapacitors), and hybrid capacitors (**Figure 1**) [7]. **Figure 1** summarizes the basic energy storage principles of supercapacitors with the classification as the basic framework and examines the research progress of electrode materials commonly used in recent years.

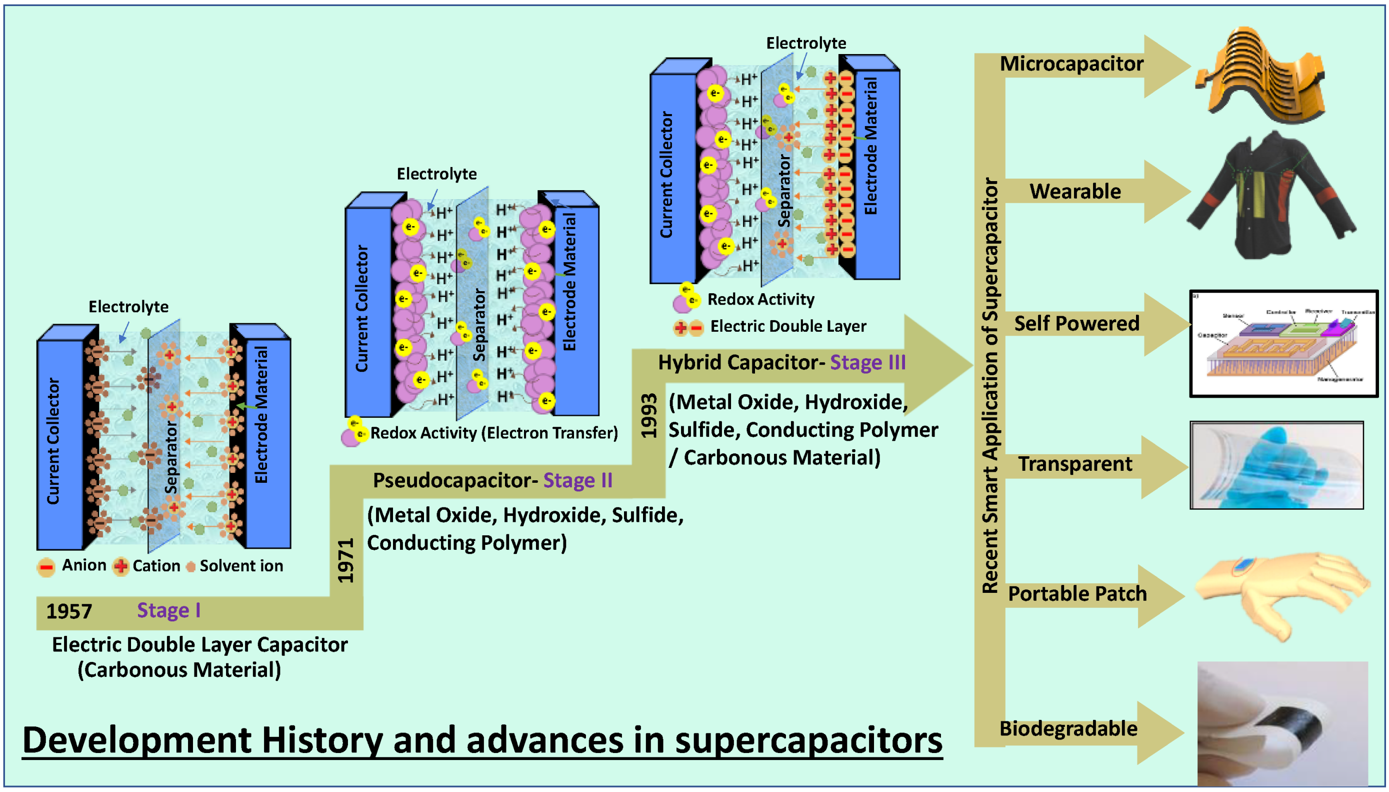

Figure 1. Classification of supercapacitors based on various electrode materials and their advanced applications.

Supercapacitors are being researched extensively in smart electronics applications such as flexible, biodegradable, transparent, wearable, flexible, on-chip, and portable energy storage. In comparison with conventional capacitors, supercapacitors use materials with a high specific surface area as electrodes [8][9]. A higher specific surface area and thinner dielectrics result in greater specific capacitance and energy density. In comparison with the rated capacitance of traditional capacitors in the range between micro and milli- Farads, the capacitance of a supercapacitor unit can reach thousands of Farads. In contrast with batteries, the charge storage mechanism of supercapacitors is based on the surface reaction of the electrode material, and there is no diffusion of ions inside the material. Therefore, supercapacitors have a better power density under the same volume. Another electrochemical characteristic that is different between supercapacitors and batteries is that the charge on the electrodes of a typical supercapacitor always increases (or decreases) linearly, resulting in voltage rise (or fall) during the charge and discharge process.

As shown in **Figure 2**, during the charge and discharge process, the cyclic voltammetry (CV) curve of the supercapacitor (**Figure 2**a) remains rectangular, whereas the current is almost constant. In addition, its galvanostatic charge-discharge (GCD) curve (**Figure 2**c) is usually inclined with a constant slope. A battery exhibits Faradaic reactions during the charge and discharge process, and its CV curve shows a clear redox peak; it maintains a constant voltage except when it is near 100% charged/discharged (TOC/EOD) (the GCD curve shows a relatively flat charge-discharge platform).

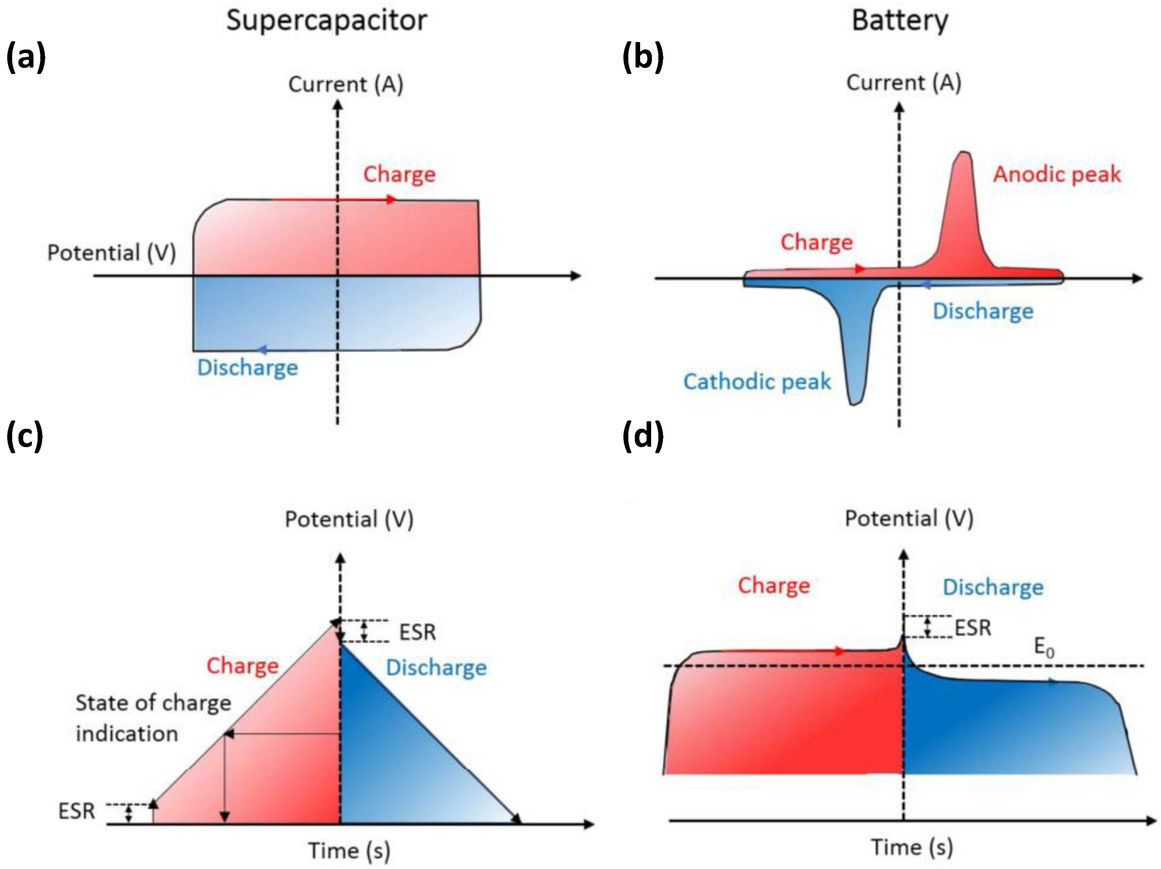

Figure 2. (**a**,**b**) cyclic voltammetry (CV) curves and (**c**,**d**) galvanostatic charge-discharge (GCD) curves of supercapacitors and batteries. Reproduced with permission [10] Copyright © 2022, Chemical Reviews.

Supercapacitors have many other advantages, such as being environmentally friendly, having a long service life, being able to operate in wide temperature ranges, and being good at retaining charge even when large currents are applied; they are widely used in consumer electronics, smart meters, and transport [7][8][9][10]. Supercapacitors have shown that they can perform very well in some applications, but there are still several shortcomings that are relevant in some applications. These include high energy density requirements and very long working times. Notably, the areas in which supercapacitors can store charge are limited to the surfaces (or near the active surface area) of the electrodes; they have lower energy density than batteries.

2. Ceramic-Based Hybrid Supercapacitors

Most metal oxides used in pseudocapacitors are often hindered by the severe aggregation of nanoparticles, low electron–proton transport, and weak conductivity between nanoparticles, leading to a lower specific capacitance in practical applications. In order to effectively address these problems, the development of hybrid electrodes by combining metal oxides with carbon materials with a high specific surface area, such as activated carbon, graphene, CNTs, and carbon aerogels, has attracted widespread attention. Various metal oxide/carbon material composite electrodes for supercapacitors are summarized in **Table 1** [11][12][13][14][15][16][17][18][19][20][21][22][23][24][25][26][27][28][29][30][31].

Table 1. Summary of various metal oxide/carbon composite electrodes for supercapacitors.

Material	Potential Window/V	Electrolyte	Specific Capacitance/F g^{-1} (Scan Rate or Current Density)	Retention/% (Cycles)	Ref.
ZrO_2 carbon nanofibers	0–1	6 M KOH	140 (1 A g^{-1})	82.6 (10,000)	[32]
$RuNi_2O_4$/rGO composites	0–1	0.5 M Na_2SO_4	792 (1 A g^{-1})	93 (10,000)	[33]
NiO/activated carbon composites	0–0.4	2 M KOH	568.7 (0.5 A g^{-1})	90.6 (5000)	[34]
$Ni_{0.25}Co_{0.25}$oxide/carbon nanofibers	−1–0	6 M KOH	431.2 (1 A g^{-1})	94 (2000)	[35]
MnO/Fe_2O_3/carbon nanofibers	0–1	6 M KOH	437 (1 A g^{-1})	94 (10,000)	[36]
ZnO/MnO/carbon nanofibers	0–1.6	6 M KOH	1080 (1 A g^{-1})	96 (800)	[37]
Au-Mn_3O_4/GO nanocomposites	−0.2–1	0.5 M H_2SO_4	475 (1 A g^{-1})	94 (10,000)	[11]
Bi_2O_3/MWCNT composites	−1.2–0.2	6 M KOH	437 (1 A g^{-1})	88.7 (3000)	[12]
NiO/MnO_2/MWCNT composites	0–0.55	2 M KOH	1320(1 A g^{-1})	93.5 (3000)	[13]
Carbon nanosheets/MnO_2/$NiCo_2O_4$ composites	0–1	1 M KOH	1254 (1 A g^{-1})	81.9 (5000)	[14]
ZrO_2/C nanocomposites	0–1	1 M H_2SO_4	214 (1.5 A g^{-1})	97 (2000)	[15]
NiO/porous amorphous carbon nanostructure	0–1.6	6 M KOH	508 (1 A g^{-1})	78 (3000)	[16]
Defective mesoporous carbon/MnO_2 nanocomposites	−0.8–0.8	1 M Na_2SO_4	292 (0.5 A g^{-1})	79 (2000)	[17]
Activated carbon/MWCNT/$ZnFe_2O_4$	−0.1–0.6	3 M KOH	609 (1 A g^{-1})	91 (10,000)	[18]

Material	Potential Window/V	Electrolyte	Specific Capacitance/F g^{-1} (Scan Rate or Current Density)	Retention/% (Cycles)	Ref.
composites					
NiO/C@CNF composites	−0.1–0.5	3 M KOH	742.2 (1 A g^{-1})	88 (5000)	[19]
N-doped carbon quantum dots/Co_3O_4 nanocomposites	−0.4–0.6	6 M KOH	1867 (1 A g^{-1})	96 (500)	[20]
Mn_3O_4/Fe_3O_4@Carbon composites	−0.4–1.2	1 M NaCl	178 (1 A g^{-1})	95 (1000)	[21]
rGO/CNTs/MnO_2 composites///	0–1.8	1 M Na_2SO_4	332.5 (0.5 A g^{-1})	89.2 (10,000)	[22]
(HPC)/polyaniline (PANI) nanowire	0–1.8	1 M H_2SO_4	1080 (1 A g^{-1})	91.6 (5000)	[23]
Cyclodextrin polymer-functionalized polyaniline (CDP)/porous carbon composites(PC)	−0.2–0.8	6 M KOH	437 (0.1 A g^{-1})	81 (5000)	[24]
MnO_2/Graphene Oxide/Polyaniline composites	0–1	1 M Na_2SO_4	512 (0.25 A g^{-1})	97 (5100)	[25]

[38] real-time ceramic arbon can ng other performances (e.g., power density). Recently, Tiwari et al. [39] synthesized highly conductive MnS_2/CNT and MnO_2/CNT core–shell heterostructures by combining two different techniques: chemical and magnetic sputtering. With the contrast in work function between MoS_2 and MnO_2, they explore the maximum potential window that can be gained by implementing the asymmetric design. Self-standing prepared electrodes, which are 3-electrode configurations, provide very high capacitances of 0.41 and 0.6 Fcm^{-2}, respectively, for MoS_2/CNT and MnO_2/CNT. The MoS_2/CNT electrode has electrostatic polarization between −0.6 and 0.2 V, whereas the MnO_2/CNT electrode has non-Faradaic charge storage between 0 and 1 V. By combining chemical and physical deposition techniques, this scalable synthesis technique allows for a massive array of edge-exposed catalytic sites available for electrode–electrolyte interaction. Hu et al. [40] synthesized $NiCoO_2$ nanosheets using CNTs to bond them together using the hydrothermal method and fabricated integrated $NiCoO_2$@CNTs@NF electrodes. These self-supporting electrodes have some advantages, such as having a structured 3D and very strong network, good conducting properties, and many sites where ions can be trapped and react quickly using a fast Faradaic redox reaction. $NiCoO_2$@CNTs@NF-integrated electrodes have excellent capacitance and stability due to the outstanding synergistic effect between $NiCoO_2$ nanosheets as Faradaic pseudocapacitance materials and CNTs as EDLC materials. The fabricated device has excellent performance because it possesses a high capacitance (151 F g^{-1} at 5 mA cm^{-2}) and outstanding capability to operate at a high rate. Guo et al. [41] developed a binary network of carbon aerogel/Ni cubic carbon electrodes with thickness- and shape-independent properties. It was achieved using a very efficient and economical route consisting of the facile polymerization of technical lignin and formaldehyde in hypersaline conditions. The porosity and degree of graphitization and carbon residues in LCAN are controlled by the ratio of $ZnCl_2$ to lignin. By precisely adjusting the ratios and combining the advantages of the LCA/Ni binary network, they thusly synthesize a cubic electrode with optimal electrochemical performance. Zhou et al. [42] used radish as a cheap catalyst and developed a facile method for synthesizing 3D carbon aerogels

incorporating MnOx nanoparticles. The combination of MnOx nanoparticles and carbon nanotubes into a supercapacitor electrode material can prove beneficial, as carbon nanotubes allow for the easy transport of ions, thus enhancing the capacity of the supercapacitor. The electrochemical performance of the carbon aerogel/MnOx composite can be enhanced by the synergistic effect between carbon nanotubes and MnOx nanoparticles. Prepared carbon aerogel-based electrodes (CAE) exhibit the highest gravimetric capacitance (GP) of 557 F g^{-1} at a current density of 1 A g^{-1} in a 3-electrode system. Carbon and pseudocapacitive materials generally have high specific capacitance and high energy density and are expected to be incorporated with carbon aerogels to produce composite materials with better electrochemical performance. The combination of carbon aerogel energy density, specific capacitance and electrical conductivity could produce composite materials with higher electrochemical performance. Kumar et al. [43] used a simple and fast microwave approach to synthesize the composite rGO@CoO within a short duration of only 90 s for developing an advanced supercapacitor electrode. The hybrid composite combines the advantages of its capacitance properties with enhanced electrochemical performance, including higher specific capacitance and excellent long-term cycling stability. Transition metal oxides with various morphologies demonstrated promising electrochemical performance along with the graphene materials through synergistic contribution from each component as well as easy electrolyte ion insertion without distortion of the nanostructure.

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