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Kamal K. Kar Editor

Handbook of Nanocomposite Supercapacitor Materials IV

Next-Generation Supercapacitors



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Dedicated to my wife, Sutapa, and my little daughter, Srishtisudha, for their loving support and patience, and my mother, late Manjubala, and my father, late Khagendranath

Preface

The global energy scene, one of the world's largest and most diversified fields, is in a state of flux. These include the moving consumption away from non-renewable energy sources, rapid deployment of major renewable energy technologies and deep decline in their costs, and a growing shift toward electricity in energy use across the globe. This power and energy system is experiencing significant changes and challenges due to transitioning from traditional power and energy networks to smart power/energy grids. As long as the energy consumption is intended to be more economical and more environment-friendly, electrochemical energy production is under serious consideration as an alternative energy/power source. In other words, a large amount of electricity can be generated from natural sources like solar, wind, and tidal energy. It is imperative to stock the produced energy since man has constrained control over these natural wonders. Batteries, fuel cells, and supercapacitors belong to the same energy storage devices, ubiquitous in our daily lives. But the supercapacitor is a step-up device in the field of energy storage. It has a lot of research and development scope in design, parts fabrication, and energy storage mechanisms.

Various types of supercapacitors have been developed, such as electrochemical double-layer capacitors (EDLCs), pseudocapacitors (redox capacitors), and capacitors. They store charges electrochemically and exhibit high power densities, moderate-to-high energy densities, high rate capabilities, long life, and safe operation. The electrode, electrolyte, separator, and current collectors are the critical parts of the supercapacitors for energy storage to determine the electrochemical properties, energy storage mechanism, and other properties of the supercapacitor devices.

Volume I, i.e., characteristics for the book series *Handbook of Nanocomposite Supercapacitor*, emphasizes the features of the capacitor, i.e., fundamental aspects; capacitor to supercapacitor; characteristics of transition metal oxides, activated carbons, graphene/reduced graphene oxide, carbon nanotubes, carbon nanofibers, and conducting polymers; characteristics of electrode materials, electrolytes, separators, and current collectors; and applications of supercapacitors.

Volume II, i.e., performance for the book series *Handbook of Nanocomposite Supercapacitor*, discusses the electrochemical properties of transition metal oxide-based electrode, activated carbon-based electrode, composite electrode based

on transition metal oxides and activated carbon, carbon nanofiber-based electrode, composite electrode based on different types of transition metal oxides and carbon nanofibers, carbon nanotube-based electrodes, combination of carbon nanotube and transition metal oxide as a hybrid electrode, graphene-based electrodes, hybrid composites based on transition metal oxides and graphene/reduced graphene oxide, electrode materials based on conducting polymers and their nanostructures, composites of conducting polymers and transition metal oxide, and comprehensive overview/recent trends of the specific capacitance and cycle life of various electrode materials used in supercapacitors, which are carbon nanofibers, carbon nanotubes, graphene/reduced graphene oxide, activated carbon, transition metal oxides, conducting polymers, and their composites. Finally, it highlights the advantages, challenges, applications, and future directions of these materials.

The performance of devices is still challenging in terms of capacitance, flexibility, cycle life, etc. These deciding factors depend on the characteristics of the materials used in the devices. The key objective is to select the right materials with new technologies and developments for the electrodes, electrolytes, separators, and current collectors, which are the essential components of supercapacitors with an aim to enhance the performance of supercapacitors. Volume III, i.e., material selection for the book series *Handbook of Nanocomposite Supercapacitor* emphasizes a comprehensive study on the fundamentals of supercapacitors, recent development of supercapacitors, material selection for electrodes, electrolytes, separators, and current collectors using Ashby chart, market trend of supercapacitors, and applications of supercapacitors.

Many significant breakthroughs have been reported in recent years through the development of these materials and novel device designs. Volume IV, i.e., next generation for the book series *Handbook of Nanocomposite Supercapacitor*, emphasizes micro-supercapacitors, shape memory supercapacitors, self-healing supercapacitors, high mass loading solid-state supercapacitors, magnetoelectric supercapacitors, atomic-layer-deposited electrodes for supercapacitor, additive manufacturing/3D printing of supercapacitor, etc.

In this book, next-generation supercapacitors, Chap. 1 discusses the fundamentals of supercapacitors, the charge storage mechanism of supercapacitors, electrochemical cell configuration (i.e., three-electrode and two-electrode systems), electrochemical measurement techniques for supercapacitor (i.e., cyclic voltammetry, constant current charge-discharge, electrochemical impedance spectroscopy, and electrochemical methods for determining the contribution of various charge storage mechanisms.

The supercapacitor has four essential components: electrode, electrolyte, current collector, and separator, in which electrode material selection is the most important factor for the charge storage mechanism. Different types of electrode materials like carbon-based electrode material, transition metal oxides, transition metal dichalcogenides, and conducting polymers are used in supercapacitor applications. Chapter 2 discusses the properties of electrode materials, nanomaterials as electrode materials (i.e., zero-dimensional nanoparticles, one-dimensional nanostructures, two-dimensional nanosheets, three-dimensional porous architectures), carbon materials

(i.e., activated carbon, carbon aerogels, carbon nanotubes, carbon nanofibers, carbon nanodot, graphene, graphene oxide, reduced graphene oxide, fullerenes), transition metal dichalcogenides (i.e., molybdenum di-sulfide, tungsten di-sulfide, cobalt di-sulfide, tin di-sulfide, titanium di-sulfide, zirconium di-sulfide, vanadium di-sulfide, molybdenum di-selenide, vanadium di-selenide, tungsten di-selenide, nickel di-selenide), transition metal oxides (i.e., ruthenium oxide, manganese dioxide, nickel oxide, nickel hydroxide, iron oxides, cobalt oxide, cobalt hydroxide, vanadium oxide, tin oxide, iridium oxide, titanium oxide, zinc oxide, molybdenum oxide, tungsten oxide, tungsten

MXenes have been recognized as front-runners in energy storage, thanks to their abundant surface functional groups, large electrochemically active surface area, redox activity, and metallic conductivity. MXenes display extraordinarily higher volumetric capacitance, making them a considerable contender in portable electronic devices. Chapter 3 discusses the current advances, achievements, and challenges in MXene-based supercapacitors, including important synthetic aspects of MXenes along with their physical and chemical characteristics.

The laser provides a single-step, low-cost, and fast processing of materials to form and integrate interdigitated electrodes for micro-supercapacitors. Chapter 4 illustrates the different parameters of the laser, laser-based processes, effect of laser–matter interactions, different materials synthesized from the laser, and the formation of micro-supercapacitors with performance details.

The performance deteriorates with an increase in the size of devices due to the internal resistance from non-active materials such as binders and additives, heating issues, and the high cost of production. To address these challenges, the designer develops electrode structures such as self-standing architectures, mesh-type electrodes, and fractal designs that can be viable solutions to enhance the performance of large-scale energy storage devices. Chapter 5 discusses the challenges in scalable-energy storage devices (i.e., degradation in performance, cost-effectiveness, heating issues, voltage imbalance, etc.), ways to address challenges for large-scale super-capacitors (i.e., geometry/electrode structure, cost-effectiveness by using industrial waste, device architecture, voltage stabilization), and various fabrication techniques (i.e., printed supercapacitors, additive nanomanufacturing, electrode production, electrolyte production, material processing, and optimization).

Numerous developments have been made in supercapacitors' three-dimensional (3D) printing. In a consistently changing technological landscape, it is important to understand how 3D printing could evolve in the future in supercapacitor technology. Chapter 6 describes the main 3D printing technologies and the relevant materials used to make supercapacitors. The chapter also discusses the prospects of 3D printing-based development of supercapacitors in the future.

Atomic layer deposition (ALD) is considered an efficient technique for depositing various kinds of films with excellent uniformity and conformity. This makes ALD an attractive choice for designing high-performance supercapacitor electrode materials possessing fast charge transfer kinetics, improved energy, and power delivery with better cycling and rate performances. Chapter 7 presents the recent advances in the use of ALD to design electrodes for supercapacitors. In addition, the present

challenges and potential opportunities for future exploration of ALD to achieve desired electrochemical performance of next-generation supercapacitors are also pointed out.

Binder restricts the electrode material's performance by increasing the contact resistance and preventing electrolytes from utilizing the whole area of the electrode. A binder-free supercapacitor is a new approach for improving the performance of supercapacitors by growing or depositing the active material on the conducting substrate. Binder-free electrode material can be fabricated by physical, thermal, and electrical methods. Chapter 8 discusses different fabrication methods (i.e., electrospinning, vacuum filtration, physical vapor deposition, thermal treatment, hydrothermal treatment, chemical bath deposition, chemical vapor deposition, atomic layer deposition, electroplating, anodization, electrophoretic deposition, etc.) and performances of binder-free electrodes.

High mass loading electrode materials are a commercial requirement of supercapacitor fabrication. At least 30% of the device weight should be posed by active electrode material to stable performance of electrochemical energy storage supercapacitor devices. Commercial-level supercapacitors require high mass loading greater than 10 mg cm⁻² or a film thickness of 150–200 μ m. High mass loading supercapacitor performance decreases because of the tortuous path of ion diffusion. Chapter 9 discusses the effect of mass loading, selective electrode materials (i.e., carbon, metal oxide, conducting polymer, MXenes, metal-organic framework, interconnected conducting porous network structure, aerogel, doping, surface modification, etc.), and electrochemical performance.

In polymer-in-salt-electrolytes, the ion transport is decoupled from the polymersegmental motion. Hence, faster and better-targeted ion transport is achieved. Special polymer hosts are required to hold salt concentration above the required threshold value for ion-cluster formation. Crosslinked starch seems to be an excellent host to hold sufficient salt in dissociated form along with flexible morphology required for commercial application and has high conductivity (>0.01 S/cm) and a wide electrochemical stability window (>2.5 V). Chapter 10 focuses on starch-based electrolytes and their performances.

Over the last few decades, transition metal oxides have been the most used materials in pseudocapacitors. The magnetic nature of these materials originates from the effective spin interaction of the materials, which can be in short- or long-range order. Fe-based materials are mostly used for magnetic applications and have also been used as pseudocapacitor electrodes. There are other magnetic transition electrodes that are being used in supercapacitors. These include iron oxide, nickel oxide, cobalt oxide, copper oxide, manganese oxide, etc. Chapter 11 deals with understanding the effect of the external magnetic field on the performance of supercapacitors fabricated using magnetically responsive materials, i.e., magnetoelectric supercapacitors. Further, a simple theoretical model is also provided chapter to explain the experimental data. A new theory was required because the conventional models used to explain the supercapacitive behavior do not have any terms which consider the possibility of changing magnetic fields and their impact on electrochemical behavior. The advancement in the technology application of micro-electronic gadgets has seen an upsurge. The progress of micro-scale devices is significantly dependent on the development of micro-scale energy storage devices with outstanding charge storage properties. In this Chap. 12, the various device architecture designs and the state of the art of it have been discussed. Further, the different device preparation methods have been discussed, outlining their advantages and disadvantages. This is followed by a short and precise discussion about the patterning, and micro-supercapacitor systems developed recently. This chapter also discusses works reporting the various applications of micro-supercapacitors in different fields.

This intelligent technology using shape memory is a primary requirement of flexible and wearable electronics. NiTi alloy and shape memory polymer are used to assemble a smart energy storage device with property shape recovery. Shape memory properties bring the device electrochemical stability, high performance, and long cycle life. Chapter 13 discusses shape memory alloys, shape memory polymers, shape memory characterization techniques, and electrochemical performances.

With the advancement of current wearable electronic gadgets, a flexible and self-healing supercapacitor is required. Flexible supercapacitors can often endure bending, and stretching stains, so mechanical damage or micro-cracks can degrade the electrochemical performance of supercapacitors. Intrinsic and extrinsic self-healing mechanisms are used during repair. Since self-healing supercapacitors are developing rapidly, still these are in their infancy because of many limitations like high cost and lower performance. Chapter 14 discusses various fabrication methods of self-healing electrode material and self-healing electrolyte materials with their electrochemical performances in supercapacitors.

The world is utilizing optics through optical fibers, data communication, processing, and fabrication of high-resolution or precise instruments. Chapter 15 deals with the applications of optics-based devices, fabrication of optical chips, transmission systems, and infrastructure, along with computational and governance requirements. Laser-based on-chip micro-supercapacitors and energy storage management facilities for clean, renewable energy are also discussed.

The use of supercapacitors is increasing in the electronics field due to their properties and sustainability. Controlling this e-waste generation by supercapacitors should be considered seriously to overcome the upcoming problem of e-waste management. Recycling supercapacitors is cost-effective and beneficial for the environment because it keeps dangerous elements out after the device has completely degraded. Chapter 16 discusses the recycling of ruthenium oxide-based supercapacitors. Sonication, chemical separation, and thermal decomposition methods were discussed. The electrochemical performance of the supercapacitor based on recycled RuO_2 material was also reported.

Therefore, this book will provide the readers with a complete and composed idea about the fundamentals of supercapacitors, the recent development of electrode materials for supercapacitors, and the design of their novel flexible solid-state devices. This book will be useful to graduate students and researchers from various fields of science and technology, who wish to learn about the recent development of supercapacitors and select the right material for high-performance supercapacitors. The editor and authors hope that readers from materials science, engineering, and technology will be benefited from reading these high-quality review articles related to the characteristics of materials and their selections used in supercapacitors. This book is not intended to be a collection of all research activities on composites worldwide, as it would be rather challenging to keep up with the pace of progress in this field. The editor would like to acknowledge many material researchers, who have contributed to the contents of the book. The editor would also like to thank all the publishers and authors for permitting us to use their published images and original work. I also take this opportunity to thank Viradasarani, Zachary, Viradasarani Natarajan, Adelheid Duhm, and the editorial team of Springer Nature for their helpful advice and guidance.

There were lean patches when I felt I would not be able to take time out and complete the book, but my wife, Sutapa, and my little daughter, Srishtisudha, played a crucial role in inspiring me to complete it. I hope that this book will attract more researchers to this field and that it will form a networking nucleus for the community. Please enjoy the book, and please communicate to the editor/authors any comments that you might have about its content.

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Contents

Intro	duction	to Supercapacitors	1
Chira	ig Mevac	la and Mausumi Mukhopadhyay	
1.1	Introdu	iction	1
1.2	Fundar	mentals of Supercapacitor	2
1.3	The Ch	narge Storage Mechanism of Supercapacitors	6
1.4	Electro	chemical Cell Configuration	8
	1.4.1	Three Electrode System	8
	1.4.2	Two Electrode System	9
1.5	Electro	ochemical Measurement Techniques	
	for Sup	percapacitor	11
	1.5.1	Cyclic Voltammetry (CV)	11
	1.5.2	Constant Current Charge–Discharge (CCCD)	12
	1.5.3	Electrochemical Impedance Spectroscopy (EIS)	13
1.6	Electro	ochemical Methods for Determining the Contribution	
	of Vari	ous Charge Storage Mechanisms	14
	1.6.1	Trasatti Method (Voltammetric Charge	
		Dependence on Scan Rate)	14
	1.6.2	Dunn Method (Current Dependence on Scan Rate	
		from the CV)	15
Refe	rences .	· · · · · · · · · · · · · · · · · · ·	17
Trad	itional H	Electrode Materials for Supercapacitor	
Appl	ications		19
Sahel	li Bera. F	Kapil Dev Verma, and Kamal K. Kar	
2.1	Introdu	iction	19
2.2	Electro	ode Materials	21
	2.2.1	Properties of Electrode Materials	21
	222	Nanomaterials as Electrode Materials	21
2.3	Materi	als for Electrodes of Supercapacitors	25
2.3	Materia 2.3.1	als for Electrodes of Supercapacitors	25 25
	Intro Chira 1.1 1.2 1.3 1.4 1.5 1.6 Refer Trad Appl Sahe 2.1 2.2	IntroductionChirag Mevad1.1Introdu1.2Fundar1.3The Cl1.4Electrod1.4.11.4.21.5Electrodfor Sup1.5.11.5.21.5.31.6Electrodof Varia1.6.11.6.2I.6.2References .Traditional IApplicationsSaheli Bera, H2.1Introdu2.2Electrod2.2.12.2.2	Introduction to Supercapacitors Chirag Mevada and Mausumi Mukhopadhyay 1.1 Introduction 1.2 Fundamentals of Supercapacitor 1.3 The Charge Storage Mechanism of Supercapacitors 1.4 Electrochemical Cell Configuration 1.4.1 Three Electrode System 1.4.2 Two Electrode System 1.5 Electrochemical Measurement Techniques for Supercapacitor 1.5.1 1.5.1 Cyclic Voltammetry (CV) 1.5.2 Constant Current Charge–Discharge (CCCD) 1.5.3 Electrochemical Impedance Spectroscopy (EIS) 1.6 Electrochemical Methods for Determining the Contribution of Various Charge Storage Mechanisms 1.6.1 1.6.1 Trasatti Method (Voltammetric Charge Dependence on Scan Rate) 1.6.2 1.6.2 Dunn Method (Current Dependence on Scan Rate from the CV)

		2.3.3	Transition Metal Oxide (TMO)	45
		2.3.4	Spinel-Based Nanostructured Materials	56
		2.3.5	Spinel-Type Oxides (MMoO ₄ (M=Fe, Ni, Co))	57
	2.4	Conclu	ision	58
	Refe	rences .		58
3	Eme Shag	rging 2 ufi Naz <i>I</i>	Materials for Supercapacitors: MXenes Ansari, Mohit Saraf, and Shaikh M. Mobin	65
	3.1	Introdu	action	66
	3.2	Synthe	tic Strategies	67
		3.2.1	HF Etching Method	67
		3.2.2	Alkali Etching Method	69
		3.2.3	Molten Salt Etching Method	70
		3.2.4	Acid/fluoride Salt or Hydrofluoride Etching	72
		3.2.5	Electrochemical Etching	73
	3.3	Structu	re and Properties of MXenes	73
	3.4	MXen	es in Supercapacitors	74
		3.4.1	MXenes as Supercapacitor Electrode Materials	75
		3.4.2	MXene-Based Composites as Supercapacitor	
			Electrode Materials	76
	3.5	Progre	ss of MXenes-Based Supercapacitor Devices	82
	3.6	Conclu	sions and Outlook	82
	Refe	rences .		84
4	Lase	r as a To	ool for Fabrication of Supercapacitor Electrodes	89
	Ravi	Nigam,	Rajesh Kumar, and Kamal K. Kar	
	4.1	Introdu	action	89
	4.2	Laser 7	Fechnology in Energy Electrodes Design	90
	4.3	Proces	sing of Laser in Carbon Materials	92
		4.3.1	Cutting	92
		4.3.2	Etching	94
		4.3.3	Ablation	94
		4.3.4	Laser Writing	95
		4.3.5	Laser Printing	97
		4.3.6	Defect Creation	99
	4.4	Laser-	Assisted Modification of Carbon Materials	99
		4.4.1	Carbonization	100
		4.4.2	Transformation of Graphite to Graphene	102
		4.4.3	Non-crystalline Carbon to Graphene	102
		4.4.4	Laser-Induced Graphene	103
		4.4.5	Reduction of Graphene Oxide	104
	4.5	Laser-l	Derived Material in Supercapacitor	106
		4.5.1	Electrochemical Double-Layer Capacitors	106
		4.5.2	Pseudocapacitors	107
		4.5.3	Hybrid Supercapacitors	108
		Duract	Laser Based Habrication of Micro supercapacitor	100

	4.7 Refer	Conclusions and Future Perspectives	116 116
5	Scala	ble Supercanacitors	123
•	Snehr and R	raj Gaur, Ajay B. Urgunde, Gaurav Bahuguna, S. Kiruthika,	125
	5.1	Introduction	124
	5.2	Challenges in Scalable Energy Storage Devices	125
		5.2.1 Degradation in Performance	125
		5.2.2 Cost-Effectiveness	126
		5.2.3 Heating Issues	126
		5.2.4 Voltage Imbalance	127
	5.3	Ways to Address Challenges for Large-Scale	
		Supercapacitors	127
		5.3.1 Geometry/Electrode Structure	127
		5.3.2 Cost-Effectiveness by Using Industrial Waste	128
		5.3.3 Device Architecture	130
		5.3.4 Voltage Stabilization	132
	5.4	Fabrication Techniques	132
		5.4.1 Printed Supercapacitors	132
		5.4.2 Additive Nanomanufacturing (ANM)	134
		5.4.3 Electrode and Electrolyte	135
		5.4.4 Material Processing and Optimization	138
	5.5	Testing of Supercapacitors	139
	5.6	Conclusions and Future Outlook	139
	Refer	ences	140
6	3D P	rinted Supercapacitors	143
	Naga	S. Korivi and Vijaya Rangari	
	6.1	Introduction	143
	6.2	Printing Methods	145
		6.2.1 Fused Deposition Modeling	145
		6.2.2 Direct Ink Writing	145
	6.3	Printable Materials for Supercapacitors	147
		6.3.1 Electrode Materials	147
		6.3.2 Electrolyte Materials	148
	6.4	Device Design	148
	6.5	Recent Progress in 3D Printing of Supercapacitors	149
		6.5.1 FDM Printed Supercapacitors	150
		6.5.2 DIW Printed 3D Supercapacitors	151
	6.6	Technology Considerations, Challenges, and Future	
		Outlook	155
		6.6.1 Choice of Printing Method	155
		6.6.2 Materials	157
		6.6.3 Use of Non-3D Printing Methods to Fabricate	
		Device Components	158

		6.6.4	Post-processing	159
		6.6.5	Device Design and Electrode Architecture	161
		6.6.6	Sustainability	161
	6.7	Conclu	isions	162
	Refe	rences .		163
7	Aton Moho and I	n <mark>ic Laye</mark> d Zahid A Din K. N	r Deposited Supercapacitor Electrodes Ansari, Soo-Hyun Kim, Arpan Dhara, andi	167
	7.1	Introdu	iction	167
	7.2	Fundar	mentals of ALD	169
	73	ALD-C	Grown Electrodes for Supercapacitors	172
	1.5	731	AI D Coating on Carbonaceous Scaffolds	173
		732	ALD Coating on Non-carbonaceous	175
		1.5.2	Three-Dimensional Scaffolds	182
	74	Conch	isions	192
	Refe	rences		192
	Refer	iences .		172
8	Bind	er-Free	Supercapacitors	195
	Kapil	l Dev Ve	rma and Kamal K. Kar	
	8.1	Introdu	action	195
	8.2	Fabrica	ation Strategies of Binder-Free Electrode	196
		8.2.1	Physical Methods	197
		8.2.2	Chemical Methods	205
		8.2.3	Electrical Methods	216
	8.3	Conclu	isions	220
	Refe	rences .		220
9	<mark>High</mark> Muke	Mass L esh Kum	oading Supercapacitorsar and Kamal K. Kar	225
	9.1	Introdu	action	226
	9.2	Effect	of Mass Loading	227
	9.3	Materi	als for High Mass Loading	229
		9.3.1	Carbon Materials	229
		9.3.2	Transition Metal Oxide	230
		9.3.3	Conducting Polymers	230
		9.3.4	Emerging Electrode Materials	230
	9.4	Electro	bde Materials Synthesis Techniques	231
		9.4.1	Interconnected Conducting Porous Network	
			Structure	232
		9.4.2	Aerogel Synthesis Techniques	232
		9.4.3	Doping and Surface Modification	233
	9.5	Electro	chemical Performance	233
	9.6	Summa	ary and Perspective	237
	Refer	rences .		241

10	Flexi	ble-Higł	n-Conducting Polymer-In-Salt-Electrolyte	
	(PISI	E) Meml	branes: A Reality Due to Crosslinked-Starch	
	Polyr	ner Hos	t	247
	Neela	am Srivas	stava	
	10.1	Introdu	ction	248
	10.2	Starch-	Based Electrolytes	252
		10.2.1	Starch as a Host Matrix for Polymer-Electrolytes	252
		10.2.2	Reasons Why Starch Has not Been as Popular	
			as It Deserves	253
		10.2.3	Possible Approaches to Rectify the Problems	
			with Starch	253
		10.2.4	Success Story of Crosslinked Starch-Based PISEs	254
	10.3	Conclu	sion	259
	Refer	ences .		260
				200
11	Mag	neto-Ele		26
	Anan	ya Chow	anury, Sudipta Biswas,	
	Abya	ya Dhar,	Joyanti Halder, Debabrata Mandal,	
	Poorr	hachandr	a Sekhar Burada, and Amreesh Chandra	200
	11.1	Introdu		26:
	11.2	Synthe	sis of Magnetic Transition Metal Oxides	260
		11.2.1	Synthesis of Fe_2O_3 Nanoleaflets	260
		11.2.2	Synthesis of Fe_2O_3 Rod-Like Structures	26
		11.2.3	Synthesis of Fe_2O_3 Nanospheres	268
	11.3	Magne	tic Electrolyte or Effect of the External Magnetic	•
		Field o	n the Electrolyte	26
		11.3.1	Introduction of Magneto-Electric Effect (MEE)	269
		11.3.2	Effect of Magnetic Field on the Electrochemical	
			Performances	269
	11.4	Origin	of Magnetic Field	273
	11.5	Explan	ation of MEE in Supercapacitor	275
		11.5.1	Magnetic Nature of the Material Used	
			as an Electrode	275
		11.5.2	Effect of the Lorentz Force on the Material	270
		11.5.3	Domains Arrangement of the Electrode Material	27
		11.5.4	Effect of the Lorentz Force on the Electrolyte	278
		11.5.5	Magneto-Hydrodynamic Effect of the Electrolyte	279
	11.6	Theore	tical Interpretation of Magneto-Electric	
		Superc	apacitors	282
		11.6.1	Existing General Theories	282
		11.6.2	Solution of Diffusion Equation	284
		11.6.3	Diffusion-Related Explanation of Magnetic	
			Supercapacitors	290
	11.7	Summa	ury	292
	Refer	ences .		293

12	Adva	ncement in the Micro-supercapacitors: Synthesis,	
	Desig	gn, and Applications	29:
	Mand	lira Majumder and Abha Misra	
	12.1	Introduction	29:
	12.2	Device Architecture Designing	29
	12.3	Brief Introduction to the Reaction Mechanism	29
	12.4	Device Fabrication Techniques	30
		12.4.1 Screen Printing for Electrode Fabrication	30
		12.4.2 Inkjet Printing for Micro-electrode Fabrication	30
		12.4.3 Lithography for Micro-electrode Fabrication	30
		12.4.4 Laser Scribing for Micro-electrode Fabrication	30
		12.4.5 Mask-Assisted Filtering for Micro-electrode	
		Fabrication	30
	12.5	Patterning of Micro-electrodes	30
	12.6	Micro-supercapacitor Systems	31
	12.7	Application of MSCs	31
		12.7.1 Energy Storage	31
		12.7.2 Integration with Various Types of Sensors	31
		12.7.3 Medical Assistant Examination	31
		12.7.4 Alternating Current (AC) Line Filtering	31
	12.8	Evaluation of Various Parameters of Supercapacitors	31
		12.8.1 Necessary Details About the System to be Reported	31
		12.8.2 Single Electrode Capacitance	31
		12.8.3 Difference of Capacitance in Three-Electrode	
		and Two-Electrode System	31
		12.8.4 Operating Voltage	32
		12.8.5 Micro- and Macro-Supercapacitors	32
		12.8.6 Cycling Stability	32
		12.8.7 Energy, Power, and Ragone Plot	32
		12.8.8 Coulombic Efficiency—Coulombic Efficiency is	
		the Factor that Determines the Rate Capability	
		of the Supercapacitor Device	32
		12.8.9 Determining the Percent of Diffusion Controlled	
		and Surface Capacitance	32
	12.9	Conclusions and Future Perspectives	32
	Refer	ences	32
13	Shap	e Memory Supercapacitors	33
	Muke	esh Kumar, Manas K. Ghorai, and Kamal K. Kar	
	13.1	Introduction	33
	13.2	Shape Memory Alloy	33
		13.2.1 High-Temperature Shape Memory Allov	33
		13.2.2 Magnetic Shape Memory Allov	33
		13.2.3 Phenomena of Transformation of Allov	33
	13.3	Shape Memory Polymer (SMP)	33

Contents

		13.3.1 Shape Memory Principle of Polymer	338
		13.3.2 Classification of SMP	338
	13.4	Shape Memory Characterization Techniques	341
	13.5	Design and Architecture of Structural Shape Memory	
		Supercapacitor	342
		13.5.1 1D Yarn/Fiber Type Supercapacitor	342
		13.5.2 Planar and 2D Shape Memory Supercapacitor	345
	13.6	Electrochemical Performance	345
	13.7	Summary and Perspective	349
	Refer	ences	351
14	Self-F	ealing Supercanacitors	357
••	Kapil	Dev Verma and Kamal K. Kar	557
	14.1	Introduction	357
	14.2	Self-healing Mechanism	359
		14.2.1 Intrinsic Self-healing	359
		14.2.2 Extrinsic Self-healing	360
	14.3	Self-healing Materials	361
		14.3.1 Self-healing Electrode for Supercapacitor Devices	361
		14.3.2 Self-healing Electrolyte for Supercapacitor	
		Devices	368
	14.4	Conclusion	373
	Refer	ences	375
1.5	0.4	- Developing and Constant and Engineering Francescol	270
15	Dovi 1	ai Kevolution with Sustainable Energy Framework	319
	15 1	Introduction	370
	15.1	Optics Read Infrastructure	380
	13.2	15.2.1 Optical China	380
		15.2.2 Optical Davides	300
		15.2.2 Optical Devices	283
		15.2.4 Entrication Aspects	384
	153	Sustainable Energy	385
	15.5	15.3.1 Implementation Policy Aspects	387
	15.4	Concluding Remarks	380
	Refer	ences	389
	Refer		507
16	Recy	cling of Supercapacitor Materials	393
	Haris	h Trivedi, Kapil Dev Verma, and Kamal K. Kar	
	16.1	Introduction	393
	16.2	Methodology of Recycling	394
		16.2.1 Important Steps in Recycling	395
		16.2.2 Processes Involved in Recycling Supercapacitors	
	16.2	Materials	395
	16.3	Recycling of Different Materials Used in Supercapacitor	- 396

	16.3.1	Nanotubes and Organic Nanocrystals Materials
		Recycling
	16.3.2	Graphene Electrode Materials Recycling
		from the Decayed Supercapacitor
16.4	Recycli	ng of RuO ₂ from Decayed Supercapacitor
	16.4.1	Pseudocapacitance of RuO ₂
	16.4.2	Material and Method
	16.4.3	Steps Involved in Recycling RuO ₂
	16.4.4	Characterization of Extracted RuO ₂ via XRD
	16.4.5	Electrochemical Characterization of RuO ₂ -Based
		Hybrid Supercapacitor
	16.4.6	The Percentage Recovery of RuO ₂
16.5	Conclus	sions
Refer	ences	
ex		

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Chapter 1 Introduction to Supercapacitors



Chirag Mevada and Mausumi Mukhopadhyay

Abstract Supercapacitors (SCs) are the essential module of uninterruptible power supplies, hybrid electric vehicles, laptops, video cameras, cellphones, wearable devices, etc. SCs are primarily categorized as electrical double-layer capacitors and pseudocapacitors according to their charge storage mechanism. Various nanostructured carbon, transition metal oxides, conducting polymers, MXenes, and metalorganic frameworks based on electroactive materials are extensively studied for practical application. Moreover, electroanalytical techniques such as cyclic voltammetry (CV), constant current charge-discharge (CCCD), and electrochemical impedance spectroscopy (EIS) are used to evaluate the performance parameters like operating potential window, specific/areal/volumetric capacitance, equivalent series resistance, time constant, energy density, and power density of the assembled device/cell. Furthermore, the contribution of different charge storage mechanisms like the capacitive and diffusion-limited processes is estimated via several electrochemical methods such as CV recorded at different scan rates to obtain the relationship between voltammetric current and scan rate, a voltammetric charge and scan rate, and step potential electrochemical spectroscopy. Additionally, the key performance metrics such as mass loading, capacitance, potential window, cycle stability, leakage current, dwelling time, equivalent series resistance, time constant, device configuration and energy, and power densities of SCs need to study carefully for practical application.

1.1 Introduction

Nowadays, renewable energy sources like solar, wind, and tidal are used to generate electricity. These resources need highly efficient energy storage devices to provide reliable, steady, and economically viable energy supplies from these reserves. Because of this, major efforts have been made to develop high-performance energy storage devices. Batteries and electrochemical capacitors are a prime area of interest

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in the field of high-performance electrical energy storage devices [1]. The chargedischarge processes of batteries generate thermochemical heat as well as reduce the cycle life due to continuous reversible redox reactions. In contrast, supercapacitors or electrochemical capacitors, or ultracapacitors are delivering excellent advantages like safe usage, fast charging-discharging, and superior cycle stability (> 100,000 cycles) compared to batteries [2]. Supercapacitors are mainly classified into two categories which are electrochemical double-layer capacitors (EDLCs), and pseudocapacitors (PCs). EDLCs use reversible ion adsorption at the interface between electrode and electrolyte to store energy therefore the key property of ELDCs includes the high specific surface area (SSA). Nanosized carbon materials are chosen as EDLCs materials which provide high SSA and good electronic conductivity. EDLCs provide high cycle stability and power densities which are characterized by rectangular cyclic voltammetry (CV) and triangular galvanostatic charge-discharge (GCD). PCs utilized faradic reactions to store energy at the electrode surface by changing its oxidation state during charging and discharging processes [3]. The fundaments and charge storage mechanism of the supercapacitor are explained in detail in the forthcoming section.

1.2 Fundamentals of Supercapacitor

The charge storage mechanism of the supercapacitor is easily understood when it is compared with the conventional capacitors. Conventional capacitors such as dielectric capacitors and electrolytic capacitors are widely used in electronic devices. The schematic illustration of conventional capacitors is displayed in Fig. 1.1. As displayed in Fig. 1.1a, the dielectric material (e.g., mica) is placed in between the two conducting plates. When the power is supplied to dielectric capacitors, the charge is stored due to an equal amount of positive charge (Q_+) and negative charge (Q_-) accumulating on both conducting plates. On the contrary, the electrolytic capacitors (Fig. 1.1b) utilize a liquid electrolyte instead of a dielectric medium, where the charge storage is accomplished via the accumulation of cations (positive ions) of electrolyte at the interface between the negative current collector and electrolyte, and an equal amount of anions (negative) are assembled at the in the interface between the positive–negative current collector and electrolyte [4].

The charge density of electrolytic capacitors is more in comparison to dielectric capacitors due to the high mobility of the electrolytic ions. Therefore, the electrolytic capacitor capacitance is generally in the range of millifarads (mF), whereas the dielectric capacitors capacitance exhibit microfarads (μ F). The amount of electrical charge storage (Q) in the conventional capacitors is proportional to the applied voltage (V) between the positive and negative conducting plates [1, 4]. Hence, the fundamental relationship between Q and ΔV is given as Eq. 1.1.

$$Q = CV \tag{1.1}$$

1 Introduction to Supercapacitors



Fig. 1.1 Conventional capacitors: a dielectric capacitors and b electrolytic capacitors

$$C = \frac{\varepsilon_0 \varepsilon_r A}{d} \tag{1.2}$$

where *Q*: stored charge in (coulombs), *V*: applied voltage between two terminals (volts), *C*: capacitance (mF or μ F), ε_0 : vacuum permittivity (8.854 × 10⁻¹² Fm⁻¹), ε_r : relative permittivity of the dielectric medium, *A*: area of the plate (m²), *d*: distance between two plates (m) or thickness of the dielectric.

The charge storage (Q) and applied voltage (V) both are time-dependent parameters so the mathematically differentiating form of Eq. 1.1 with respect to time,

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = C\frac{\mathrm{d}V}{\mathrm{d}t} + V\frac{\mathrm{d}C}{\mathrm{d}t} = C\frac{\mathrm{d}V}{\mathrm{d}t} \tag{1.3}$$

On the left side,

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = \frac{\mathrm{d}i}{\mathrm{d}t} \tag{1.4}$$

Further modifying Eq. 1.4 based on the charge–discharge curve;

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = i \tag{1.5}$$

Thus, Eq. 1.3 is simplified as:

$$i = C \frac{dV}{dt} \tag{1.6}$$

If the applied voltage varies linearly with time,

$$V = V_0 + \Delta t \tag{1.7}$$

where V_0 : initial voltage which is equal to zero, Δ : scan rate or sweep rate (speed of the potential change, mVs⁻¹) and t is the time. Then,

$$\frac{\mathrm{d}V}{\mathrm{d}t} = \Delta \tag{1.8}$$

Substituting them into Eq. 1.6 yields,

$$i = C\Delta \tag{1.9}$$

Equation 1.9 signify that the current (i) passing through a capacitor is a strong function of scan rate (Δ) and more importantly, it is independent of the applied voltage (V). Additionally, the plot of the current versus voltage (i vs. V) for various scan rates yields a rectangular shape which is known as a cyclic voltammogram (CV) (Fig. 1.2a). CV is the electroanalytical technique that is used to justify the capacitive behavior of electrode material or device. The voltage in the three-electrode configuration is referred to as the electrode potential. Thus, the plot of applied potential (V) against the charging–discharging time (t) at a constant current gives a triangular shape of the curve (V vs. t) as displayed in Fig. 1.2b.

This technique is widely known as constant current charge–discharge (CCCD) or galvanostatic charging–discharging (GCD) which is a reliable and accurate method for estimating the capacitance and ohmic drop (*IR* drop) of the capacitor electrode or device [5]. Both electrochemical measurements (CV and CCCD) methods are discussed in more detail in the forthcoming section. Furthermore, the amount of energy stored and delivered by the capacitor can be evaluated from the CCCD curves of the device. The triangle area of the working diagram of CCCD curves shown in Fig. 1.2b is utilized to evaluate the energy store [1].



Fig. 1.2 a CV curves at various scan rates and b CCCD curves at various current densities

1 Introduction to Supercapacitors

$$E = \int_{0}^{Q} V \mathrm{d}Q \tag{1.10}$$

Now, substituting Eq. 1.1 into Eq. 1.10 gives,

$$E = \int_{0}^{Q} \frac{Q}{C} dQ = \frac{Q^{2}}{2C} = \frac{QV}{2} = \frac{CV^{2}}{2}$$
(1.11)

where *E* is the energy density of the device (volumetrically: Wh L⁻¹ or gravimetrically: Wh kg⁻¹) which demonstrates the amount of energy stored in the device during charging and similarly the power density (*P*) (W L⁻¹ or W kg⁻¹) from the device can be obtained by dividing E by the time needed to fully discharge of device excluding ohmic resistance (*iR* drop) [3]. Thus,

$$P = \frac{E}{\Delta t} \tag{1.12}$$

However, the maximum power output of the device is evaluated using the shortest discharging time. The current transfer via circuit is given by I = V/R, where *R* is the internal resistance or also referred to as equivalent series resistance (ESR). When the power source is connected to a load, $R = R_L + \text{ESR}$. The power transmitted from the source to the load is given by $P = iV = i^2 R_L$ [4]. Thus,

$$P = \left(\frac{V}{R_L + ESR}\right)^2 R_L \tag{1.13}$$

The maximum power (P_{max}) output can be reached when $R_{\text{L}} = \text{ESR}$. Hence, Eq. 1.13 can be converted to:

$$P_{\max} = \left(\frac{V}{ESR + ESR}\right)^2 ESR = \frac{V^2}{4ESR}$$
(1.14)

 P_{max} is a function of applied voltage and ESR but is independent of the capacitance of the device. However, the energy density is the strong function of the capacitance of the device [6]. Additionally, the shortest discharge time (t_{min}) can also evaluate by putting Eq. 1.14 into Eq. 1.12,

$$t_{\min} = \frac{CV^2}{2P_{\max}} = \frac{CV^2}{2} \times \frac{4ESR}{V^2} = 2CESR$$
 (1.15)

Based on the above mention Eq. 1.15, the discharge time or time constant (τ) of the device is the ratio of energy density to power density which can be simply