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Kamal K. Kar *Editor*

Handbook of Nanocomposite Supercapacitor Materials IV

Next-Generation Supercapacitors

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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), and spinel-based nanostructured materials.

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 supercapacitors (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 μm. 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 polymer-segmental 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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About the Editor

Prof. Kamal K. Kar Ph.D. Professor Kar pursued higher studies at the Indian Institute of Technology Kharagpur, India, and Iowa State University, USA, before joining as a Lecturer in the Department of Mechanical Engineering and Interdisciplinary Programme in Materials Science at IIT Kanpur in 2001. He was a BOYSCAST Fellow in the Department of Mechanical Engineering, Massachusetts Institute of Technology, USA, in 2003. He is currently holding the Champa Devi Gangwal Chair Professor of the Institute. Before this, he also had the Umang Gupta Institute Chair Professor (2015–2018) at IIT Kanpur. He is the former Head of the Interdisciplinary Programme in Materials Science from 2011 to 2014, and Founding Chairman of the Indian Society for Advancement of Materials and Process Engineering Kanpur Chapter from 2006 to 2011.

Professor Kar is an active researcher in the broad areas of nanostructured carbon materials, nanocomposites, functionally graded materials, nanopolymers, and smart materials for structural, energy, water, and biomedical applications. His research works have been recognized through the office of the Department of Science and Technology, Ministry of Human Resource and Development, National Leather Development Programme, Indian Institute of Technology

Kanpur, Defence Research and Development Organisation, Indian Space Research Organization, Department of Atomic Energy, Department of Biotechnology, Council of Scientific and Industrial Research, Aeronautical Development Establishment, Aeronautics Research and Development Board, Defence Materials and Stores Research and Development Establishment, Hindustan Aeronautics Limited, Kanpur, Danone Research and Development Department of Beverages Division, France, Indian Science Congress Association, Indian National Academy of Engineering, and many more from India.

Professor Kar is the Editor-in-Chief of *Polymers and Polymeric Composites: A Reference Series* published by Springer Nature, Member of the Editorial Board of *SPE Polymers* published by Wiley, *Advanced Manufacturing: Polymer and Composites Science* published by Taylor & Francis Group, and *International Journal of Plastics Technology* published by Springer Nature and many more.

Professor Kar has more than 300 papers in international refereed journals, 135 conference papers, 12 books on nanomaterials and their nanocomposites, three special issues on polymer composites, 100+ review articles/book chapters, and more than 65 national and international patents to his credits; some of these have over 200 citations. He has guided 35 doctoral students and 100 master students so far. Currently, seven doctoral students, two master students, and few visitors are working in his group, Advanced Nanoengineering Materials Laboratory.

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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 metal–organic 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 charge–discharge 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 (μF). 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.

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

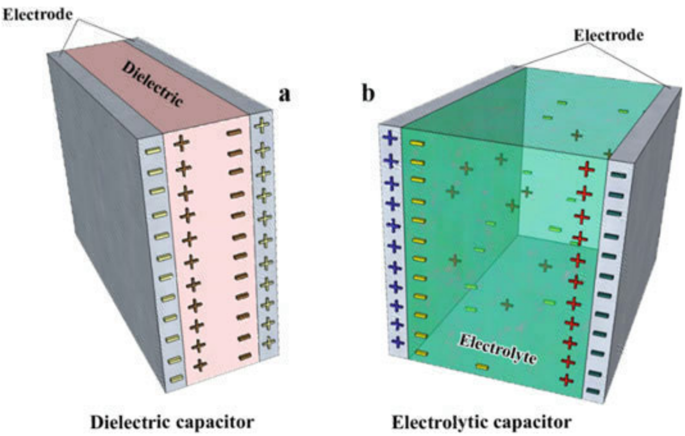

Fig. 1.1 Conventional capacitors: **a** dielectric capacitors and **b** electrolytic capacitors

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

where Q: stored charge in (coulombs), V: applied voltage between two terminals (volts), C: capacitance (mF or μF), ε_0: vacuum permittivity (8.854×10^{-12} Fm^{-1}), ε_r: relative permittivity of the dielectric medium, A: area of the plate (m^2), 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,

$$\frac{dQ}{dt} = C\frac{dV}{dt} + V\frac{dC}{dt} = C\frac{dV}{dt} \tag{1.3}$$

On the left side,

$$\frac{dQ}{dt} = \frac{di}{dt} \tag{1.4}$$

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

$$\frac{dQ}{dt} = i \tag{1.5}$$

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].

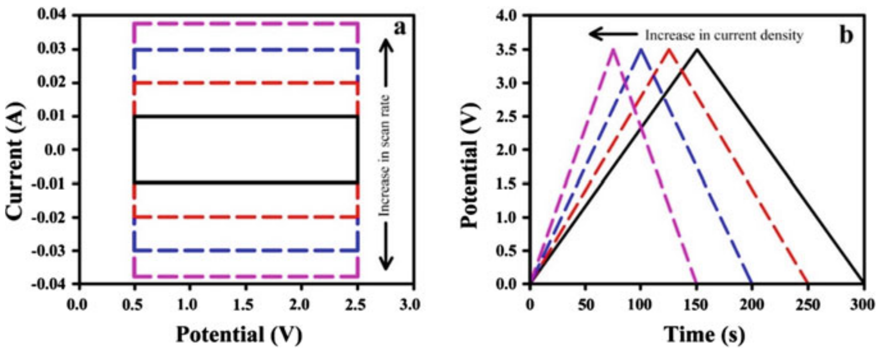

Fig. 1.2 **a** CV curves at various scan rates and **b** CCCD curves at various current densities

$$E = \int_0^Q V \mathrm{d}Q \tag{1.10}$$

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

$$E = \int_0^Q \frac{Q}{C} \mathrm{d}Q = \frac{Q^2}{2C} = \frac{QV}{2} = \frac{CV^2}{2} \tag{1.11}$$

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 $R_L = \text{ESR}$. Hence, Eq. 1.13 can be converted to:

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

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,

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

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