Polymers in Energy Conversion and Storage

EDITED BY

Inamuddin
Mohd Imran Ahamed
Rajender Boddula
Tariq Altalhi

CRC Press
Taylor & Francis Group

Polymers in Energy Conversion and Storage

Polymers in Energy Conversion and Storage

Edited by
Inamuddin
Mohd Imran Ahamed
Rajender Boddula
Tariq Altalhi


CRC Press
Taylor & Francis Group
Boca Raton London New York

CRC Press is an imprint of the
Taylor & Francis Group, an **informa** business

First edition published [2022]
by CRC Press
6000 Broken Sound Parkway NW, Suite 300, Boca Raton, FL 33487-2742

and by CRC Press
2 Park Square, Milton Park, Abingdon, Oxon, OX14 4RN

CRC Press is an imprint of Taylor & Francis Group, LLC

Library of Congress Cataloging-in-Publication Data
Names: Inamuddin, 1980- editor. | Ahamed, Mohd Imran, editor. | Boddula, Rajender, editor. | Altalhi, Tariq, editor.
Title: Polymers in energy conversion and storage / edited by Inamuddin, Mohd Imran Ahamed, Rajender Boddula, Tariq A Altalhi.
Description: First edition. | Boca Raton : Taylor and Francis, 2022. | Includes bibliographical references and index.
Identifiers: LCCN 2021055547 | ISBN 9780367770815 (hardback) | ISBN 9780367770891 (paperback) | ISBN 9781003169727 (ebook)
Subjects: LCSH: Electric batteries--Materials. | Energy storage--Materials. | Capacitors--Materials. | Energy conversion. | Polymers--Electric properties. | Polyelectrolytes. | Conducting polymers.
Classification: LCC TK2945.P65 P66 2022 | DDC 621.31/242--dc23/eng/20220105
LC record available at https://lccn.loc.gov/2021055547

ISBN: 978-0-367-77081-5 (hbk)
ISBN: 978-0-367-77089-1 (pbk)
ISBN: 978-1-003-16972-7 (ebk)

DOI: 10.1201/9781003169727

Typeset in Times
by SPi Technologies India Pvt Ltd (Straive)

Contents

Preface

Research and development activities in energy conversion and storage play a significant role in our daily lives owing to the rising interest in clean energy technologies to alleviate the fossil-fuel crisis. A variety of materials, including polymers, inorganic materials, and carbons, have been studied in energy conversion and storage applications. Among them, polymers have been extensively utilized due to their low cost, softness, ductility, and flexibility compared to carbon and inorganic materials. The polymers can also be conveniently used as binders, separators, electrolytes, and so on for additional applications in energy fields compared to inorganic materials and carbons. This book explores the wide range of applicability of polymers in energy conversion and storage. The potential applications include hydrogen production, solar cells, photovoltaics, water splitting, fuel cells, supercapacitors, and batteries. This book provides in-depth literature on the applicability of polymers in energy conversion and storage, its history and progress, fabrication techniques, and potential applications. It brings together panels of highly accomplished experts working in the field of polymeric materials for energy conversion and storage and will be an invaluable guide to students, professors, scientists, and R&D industrial experts working in the field of energy conversion and storage.

Chapter 1 covers the history and progress of polymer materials used in several energy applications divided into energy storage and conversion. Polymers are used in supercapacitors, batteries, fuel cells, and solar cells. Conducting polymers exhibit semiconductor-like properties, and they have emerged as fascinating materials for the fabrication of electronic devices.

Chapter 2 highlights the recent advancements of various polymer-based electrolytes employed in supercapacitor applications, namely: solid polymer electrolytes; gel polymer electrolytes including hydrogels and organogels; ionogel-based polymer electrolytes, proton-conducting polymer electrolytes, and polyelectrolytes. In addition,, the observations have been analyzed to interpret their practicability in designing smart, flexible, and multifunctional supercapacitors.

Chapter 3 discusses recently developed polyaniline-based electrode materials used for supercapacitor applications. To overcome, the short cycle life of polyaniline and the low specific capacity of carbon materials, metal compounds have been included as the third component to obtain ternary nanocomposites for interesting applications in the development of new supercapacitors.

Chapter 4 discusses different covalent and non-covalent approaches utilized for synthesizing self-healing gel electrolytes. The autonomous self-restoration abilities, ionic conductivities, and elongation efficiencies of various gel electrolytes, and their application in integrated flexible supercapacitors, are summarized. Also, the abilities of redox mediator doped gel electrolytes for overall augmentation in capacitance are highlighted.

Chapter 5 provides a detailed discussion of the operating mechanism of different types of polymer-based nanogenerators. The focus of the study has been on energy-harvesting device designs with polymer materials and combinations of polymer nanogenerators employed in a wide range of applications. The advantages and importance of polymer nanogenerators are highlighted with their performance.

Chapter 6 presents the concepts of piezo/pyroelectric effects, their figures of merit (FOM), measurement tools, and the materials that exhibit these properties. The various types of piezo/pyroelectric polymers, co-polymers, fillers, and composites are discussed along with an emphasis on their applications in energy harvesting, its principles, methods, and FOM.

Chapter 7 reports on the recent advances in polymers and their composites for solar cells. Polymers are used to fabricate flexible substrates, or pore-forming for photoanodes and cathodes, as well as solidify the electrolytes. Polymers showed significantly enhanced long-term stability of solar cell devices which opens the way for their practical applications.

Chapter 8 overviews various aspects of the polymer-based systems used both as electrode materials as well as ion exchange membranes in different fuel cells. It gives a detailed account of polymers and their composites utilized to accomplish a high power and energy density while also overcoming the shortcomings of currently used materials.

Chapter 9 describes the various characteristics of a solid polymer electrolyte including ionic conductivity, glass transition temperature, degree of crystallinity, and crystal growth. Further, various recent works implementing solid polymer electrolytes in rechargeable batteries are highlighted by discussing the existing issues and their possible solutions.

Chapter 10 details polymer electrolytes based on ionic conductivity. Also, the role of plasticizers, that is, organic solvents and ionic liquids in polymer electrolytes, as well as types of batteries and their parameters, are discussed in detail. Finally, the major focus is on the electrochemical measurements of polymer electrolytes for efficient polymer batteries.

Chapter 11 describes the synthesis and properties (electronic, optical, mechanical, and physical) of polymer semiconductors. It also collects the main techniques employed to study these materials (physicochemical, electro, and optical characterization). The significant applications and their highlighted features are discussed in detail.

Chapter 12 discusses the fabrication of organic polymer-based photovoltaic devices for the aim of converting sunlight into electricity. The working principle of the device,

J-V characteristics, device architecture, the effect of various factors in the operating process, future possibilities in the enhancement of power conversion efficiency, and the scope for commercialization are discussed in detail.

Chapter 13 discusses the new field of polymer application in wearable devices. Their most important properties such as stretchability, electrical conductivity, and thermoelectric properties are discussed. Conductive polymers, carbon materials, piezoelectric elastomer polymers, chitin and chitosan, rare earth nanoparticles, and composites of these materials are focused on.

Chapter 14 details various polymers and their conjugate classes that allow the manufacturing of cost-effective, lightweight, and flexible devices with remarkable applications in organic photovoltaics, organic field-effect transistors, organic light-emitting diodes, and so on. It discusses the integration of various conjugated polymers in organic electronics.

Chapter 15 summarizes recent progress in polymer thermoelectrics. It highlights the strategies for improving the thermoelectric properties of polymers by engineering the Seebeck coefficient, the electrical conductivity, and the thermal conductivity of polymers and polymer-based composites.

Chapter 16 discusses various types of polymer-based hydrogen storage systems with a focus on their mechanism of action. The gas sorption measurement techniques are also briefly covered. The primary goal is to outline the synthesis methods, benefits, and drawbacks of several polymeric materials utilized in hydrogen storage.

Chapter 17 reports on how to use water splitting applications to generate hydrogen and oxygen gases. Since materials used in water-splitting applications are not very effective, this chapter focuses on recent advances and increasing the efficiency of water-splitting processes with polymers and their composites.

1 History and Progress of Polymers for Energy Applications

Mohammad R. Thalji
Independent Researcher, Amman, Jordan

Gomaa A. M. Ali
Al–Azhar University, Assiut, Egypt

Kwok Feng Chong
Universiti Malaysia Pahang, Gambang, Malaysia

CONTENTS

1.1 INTRODUCTION: HISTORICAL PERSPECTIVE OF POLYMERS IN THE ENERGY FIELD

Polymer materials have been considered the golden gateway to the future, which deals with developing many novel materials to suit our daily lives. Polymer materials are essential in energy concepts with a wide range of applications, including semiconductors [1, 2], light-emitting diodes (LEDs) [3], flexible supercapacitors [4], flexible solar cells [5], and fuel cells [6]. Berzelius (in 1930) coined the term "polymer" to define molecules that contained the repeatedly arranged atomic groups [7]. Over time, the term came to refer to larger molecules when it was applied to long macromolecules composed of various entities (monomers) [8]. The period 1920–1940 was regarded as a golden age in the development of synthetic polymers, during which new monomers were synthesized from abundant raw materials [9]. Simultaneously, the polymerization and polycondensation processes were refined to improve their efficiency. New synthetic methods have been developed to enhance the characterization of polymer macromolecules. This enabled the creation of polymers with distinct physico-chemical characteristics by modifying the arrangement of their chains.

Polymer material has long been considered to be an insulating material. Typically, it was employed in insulating cables in electronic systems, and it was uncommon to use it as an electrode material for conducting [10]. As a result, since the discovery of polyacetylene in 1977, the growth of conducting polymers has quickly piqued the interest of both academia and industry [11]. Conducting polymers are promising energy materials due to their electrical conductivity and reversible

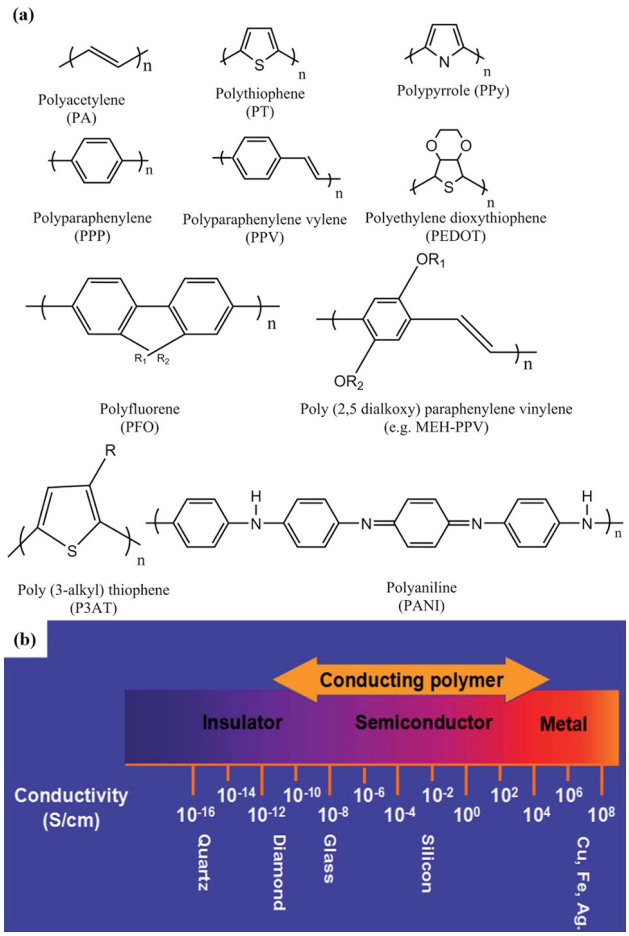

FIGURE 1.1 (a) Chemical formulas of some conducting polymers. (b) Electrical conductivity range of conducting polymers [12].

DOI: 10.1201/9781003169727-1

electrochemical performance [12]. Polyaniline (PANI), polythiophene (PT), polypyrrole (PPY), poly(ethylene dioxythiophene) (PEDOT), and poly(3-hexylthiophene) (P3HT) are some examples of the conjugated double bonds conducting polymers (Figure 1.1a). They have sp^2 in their chemical structure, facilitating charge transport and improving their electrochemical and conductivity properties (Figure 1.1b).

These polymers exhibit high potentials as electrodes for various energy devices. Although polymer materials have broad applications, this chapter will focus on their energy (conversion and storage).

1.2 POLYMER MATERIALS FOR ENERGY STORAGE APPLICATIONS

The development of a novel electrode material with a large electrochemically active surface area [13], excellent porosity [14], high conductivity [15], and pseudocapacitive properties [16] is the primary key to improving the electrochemical performance of energy storage systems. With the development of supercapacitors, some new materials have appeared gradually. Research interest has expanded beyond numerous conducting polymer materials in recent years, focusing on developing distinct electrode materials for electrochemical capacitors and batteries.

Although batteries are the most common energy source in each field, they have some limitations in the life cycle and power performance [17, 18]. Supercapacitors (SCs), known as electrochemical capacitors and ultracapacitors, are classified as energy storage devices with a high power density and long charge–discharge cycles [15, 19–21]. SCs, as shown in Figure 1.2, have a distinct Ragone plot position that bridges the gap between batteries and capacitors [22]. Also, when compared to a conventional capacitor, SCs have a higher specific energy density. Furthermore, SCs have a higher specific power density than batteries because of their unique charge storage mechanism.

Electrical double-layer capacitors (EDLCs) and faradaic pseudocapacitors (PCs) are the two main types of SCs [23]. EDLCs store electrical charges at the electrode–electrolyte interface using electrostatic force rather than electrochemical reactions on the electrode surface (Figure 1.3a). Carbon-based materials like carbon nanotubes (CNTs), carbon fibers, carbide-derived carbons, activated carbon, and graphene are commonly used as electrode materials for EDLCs [13–15, 24, 25]. Despite having a high power density and fantastic charge–discharge cycling stability, carbon-based materials have a low energy density [26]. Metal oxides, metal sulfides, and conducting polymers have been investigated as the electrode for pseudocapacitors to improve the specific capacitance and energy density of PCs [4, 20, 21, 27–32]. In PCs, energy storage is derived from reversible redox reactions at the electrolyte and electroactive interface. Because metal oxides have multiple oxidation states for redox charge transfer reactions, PCs can typically yield higher energy density than EDLCs.

Conducting polymers belong to pseudocapacitive electrode material that has been widely investigated for various energy storage applications like supercapacitors and batteries. This is associated with high energy density, redox-storage capability, relatively high conductivity, and large voltage windows [29, 33, 34]. PANI is an intrinsic polymer commonly used as electrode material in electrochemical energy storage applications. It has many distinguishing characteristics, including high conductivity and excellent electrochemical performance. Despite these benefits, it is prone to rapid performance degradation due to repeated charge–discharge cycles. To address this issue, carbon-based materials were

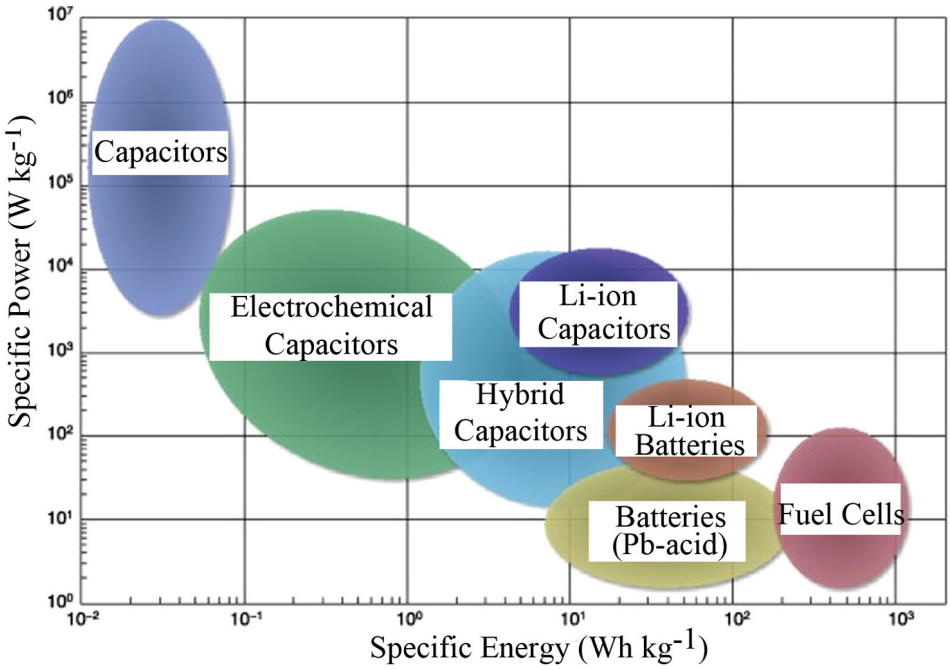

FIGURE 1.2 Ragone plot for energy storage systems [22].

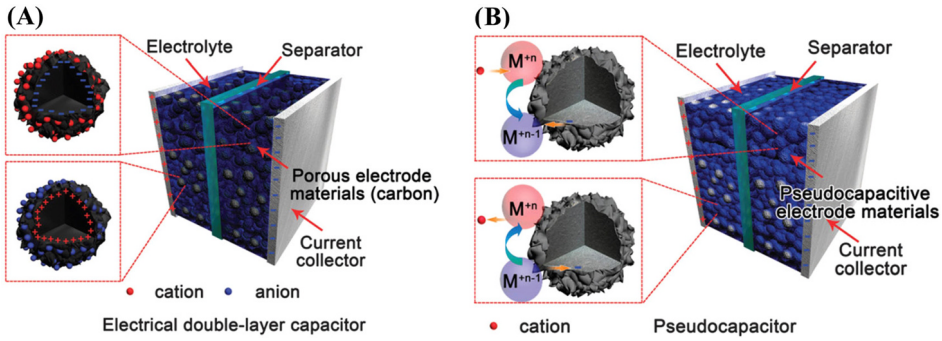

FIGURE 1.3 Representative diagrams for (a) EDLCs and (b) PCs [23].

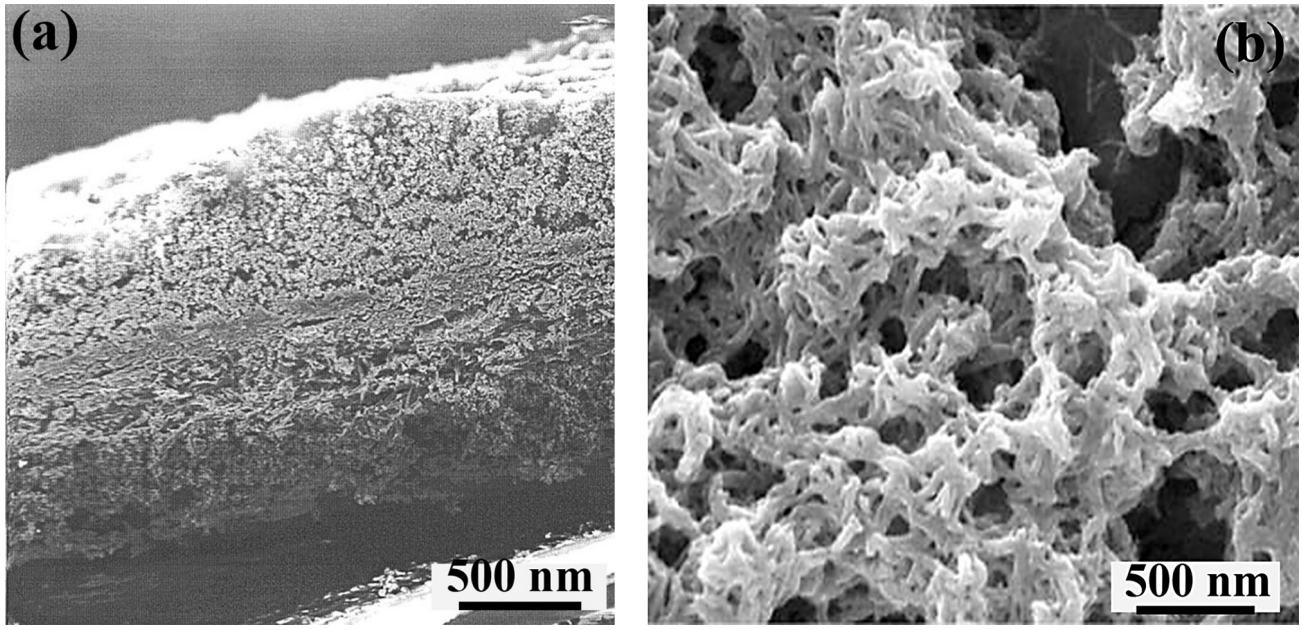

FIGURE 1.4 Scanning electron microscopy image of (a) a PANI-coated carbon paper electrode in cross-section, and (b) a PANI film fabricated by the pulse galvanostatic method (PGM) in 0.5 M H_2SO_4 and 0.2 M aniline [35].

combined with PANI material to form a novel composite that contributed to the reinforced PANI stability and enhanced the specific capacitance. For instance, Fusalba et al. synthesized a highly porous PANI film 250 mm thick (Figure 1.4a), and used it as the active material in a supercapacitor device with a nonaqueous electrolyte (1 M Et_4NBF_4/ACN) [35]. This increased the potential window in an aqueous solution from 0.75 to 1.0 V.

A low-frequency capacitance of 3 F cm^{-2} (150 F g^{-1}) was achieved in the as-prepared film. Furthermore, the PANI–PANI capacitor's cycling stability was low for the first 60 cycles (the loss of charge accounts for approximately 25% of the initial charge). In another study, Zhou et al. obtained a capacitance value of 609 F g^{-1} and an energy density of 26.8 W h kg^{-1} for a nanofibrous PANI capacitor at 1.5 mA cm^{-2} (Figure 1.4b) [36]. According to Zhou et al., the outstanding capacitance is due to a highly porous nanofibrous architecture that provides a high surface area and a great charge-transfer rate, allowing it to be a promising electrode material supercapacitor. Liu and his co-workers [37] used *in situ* aqueous polymerization to create porous PANI, and they compared its performance to that of as-prepared nonporous PANI. As shown in Figure 1.5a and b, the porous PANI had a more random pore arrangement than the nonporous PANI.

Furthermore, under 10 mA g^{-1}, the porous PANI had a specific capacitance of 837 F g^{-1}, much higher than the nonporous ones (519 F g^{-1}) (Figure 1.5c). The porous electrode exhibits high long-cycle stability and high-rate capability (Figure 1.5d). The porous PANI's notable electrochemical performance is assigned to its meso/macropores with a remarkable surface area (211 m^2 g^{-1}), compared to nonporous ones (6.0 m^2 g^{-1}), which facilitates ion transport to entire surfaces.

A flexible supercapacitor was made from polypyrrole as electrode material by creating hollow polypyrrole/cellulose hybrid hydrogels using a simple electrochemical deposition strategy on an Ni current collector (Figure 1.6a) [38]. The symmetric supercapacitor device assembly (Figure 1.6b) has a high capacitance, energy density, and capacitance retention of 255 F g^{-1}, 20.4 W h kg^{-1}, and 80%, respectively.

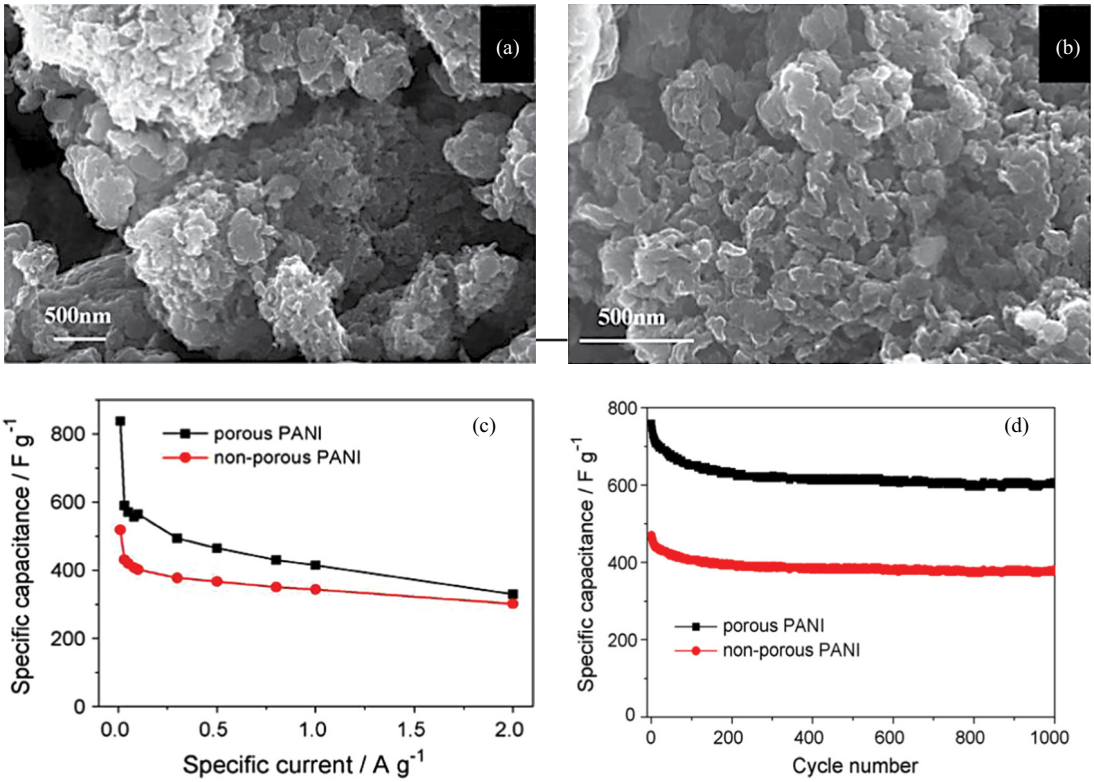

FIGURE 1.5 Scanning electron microscopy images of the (a) nonporous PANI and (b) porous PANI. (c) Specific capacitances and (d) cycle stabilities of the porous and the nonporous PANI (Liu et al. [37] with permission).

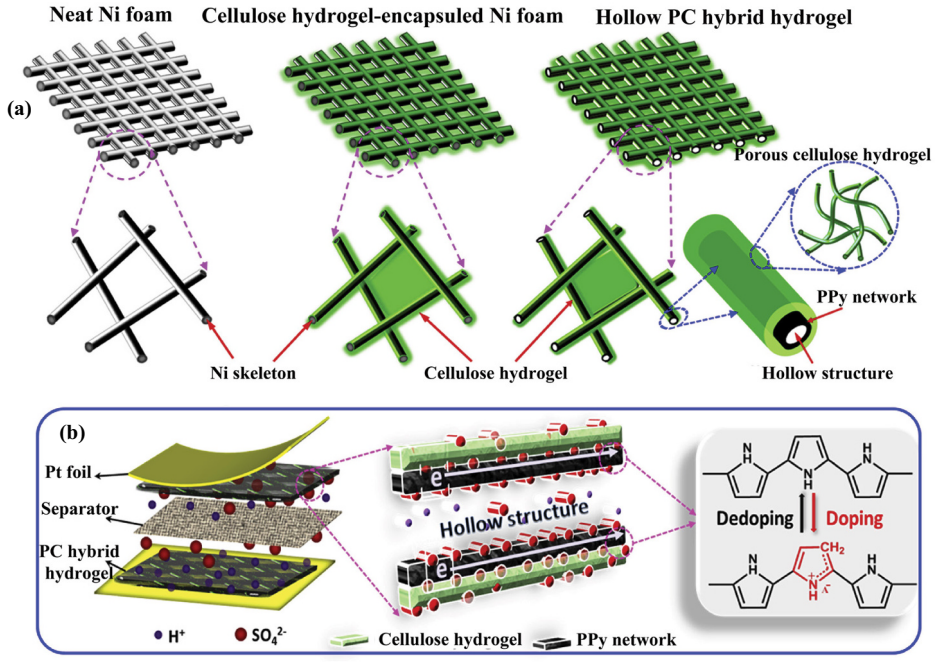

FIGURE 1.6 (a) The synthetic path and (b) the proposed electrochemical mechanism for the hollow polypyrrole/cellulose hybrid hydrogel (Zhang et al. [38] with permission).

This improvement can be attributed to cellulose hydrogel, which prevents PPy volume shrinkage and expansion during the electrochemical processes. Furthermore, its biphase porous and hollow structure can improve electrolyte ion accessibility and efficient interfacial electrochemical reaction kinetics, resulting in enhanced charge storage. As shown in Figure 1.6b, the inner phase of the polypyrrole network provides a fast electron transfer throughout the hybrid hydrogel, while the outer phase of the cellulose hydrogel is accountable for efficient ion transport and superior mechanical performance.

The insertion of carbon-based materials within conducting polymers plays a critical part in improving overall electrochemical performance. Special electrode capacity and cycling stability can be enhanced synergistically by integrating all materials for effective energy storage applications. Feng et al., for instance, reported that graphite oxide had been modified to produce composites of polypyrrole/graphite oxide using *in situ* polymerization [30]. The specific capacitance of the as-fabricated electrode was 202 F g^{-1} (a three-electrode system) and 87 F g^{-1} (a two-electrode system) at 1 A g^{-1}. The retention rate of capacity was 83.8% after 1000 cycles.

Polyindole/carbon black (PIn/CB) composite has been used as a supercapacitor electrode. Incorporating CB into the PIn improves its capacitive performance while increasing energy and power densities. Electrodes with PIn, CB, and polyvinylidene difluoride ratios of 80 wt.%, 10 wt.%, and 10 wt.%, respectively were prepared [39]. The PIn has a continuously interlinked globular morphology, as seen in the field emission scanning electron microscopy (FESEM) image (Figure 1.7a). Furthermore, as shown in Figure 1.7b, the PIn/CB composite has similar globular structures with tiny particles that are identified as CB particles. At 1.0 A g^{-1}, the authors reported a Coulombic efficiency of 89.1 and 91.1% of polyindole and polyindole/carbon black, respectively. Compared with pure polyindole (112 F g^{-1}), the composite showed an improved specific capacitance of 193 F g^{-1} at 1 A g^{-1}. Carbon's amorphous and conducting nature facilitates charge transport within the electrode material. The designable functional groups able to interact chemically with the polyindole chains facilitate the synergy of the polyindole/carbon black composite.

In another work, graphene oxide (GO) was premixed with Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) before being bar-coated on a flexible polyvinylidene fluoride current collector to create a highly flexible rGO-PEDOT/PSS electrode (Figure 1.8a) that achieved an areal capacitance of 448 mF cm^{-2} at 10 mV s^{-1} [41]. However, the GO material was agglomerated by this strategy, which was detrimental to the composite's performance (Figure 1.8b). To address this issue, a PPy/graphene composite was developed to prevent graphene sheet agglomeration (Figures 1.8c and d), in which the PPy works as gaps between graphene sheets and improves the electrolyte/electrode interface for ion transport and charge storage performance [40]. Due to the two components' synergistic effect, the resulting supercapacitor exhibited a high mechanical flexibility film (Figure 1.8e).

The carbon-based supercapacitors and conducting polymers have shown improvements in electrochemical performance, as well as flexibility. However, their performance for practical applications remains far from what is expected. Transitional metal oxides were recently admitted as an effective strategy based on their high capacities, and their electrical conductivity is relatively high. For instance, a remarkable pseudocapacitive performance of 2055 F g^{-1} at 1 A g^{-1} with outstanding cycling stability (90% retention after 5000 long-term cycles) was obtained by a supercapacitor of the $NiCo_2O_4$/PPy nanostructure that was grown on a hemp-derived carbon fiber (HDC) [42]. Polypyrrole was employed to improve the conductivity by hastening the electron transfer of $NiCo_2O_4$. As shown in Figure 1.9c, the symmetric (wire-type) supercapacitor was built utilizing NaOH/PVA as a solid electrolyte and HDC@$NiCo_2O_4$@PPy fiber composites as the current electrode. The symmetric supercapacitor had a power density of 0.5 kW kg^{-1} and a considerable energy density of 17.5 W h kg^{-1}.

Polyaniline was also employed in the presence of $CuCo_2S_4$ nanosheets on carbon cloth, as shown in Figure 1.10a, to improve the electrical performance of $CuCo_2S_4$ nanosheets via chemical polymerization of aniline [43]. At 1 A g^{-1}, the pure $CuCo_2S_4$ electrode achieved a capacitance value of 780 F g^{-1}. The electrode significantly improved after compositing ($CuCo_2S_4$/polyaniline) to the capacitance value of 920 F g^{-1}. Furthermore, the capacitance retention

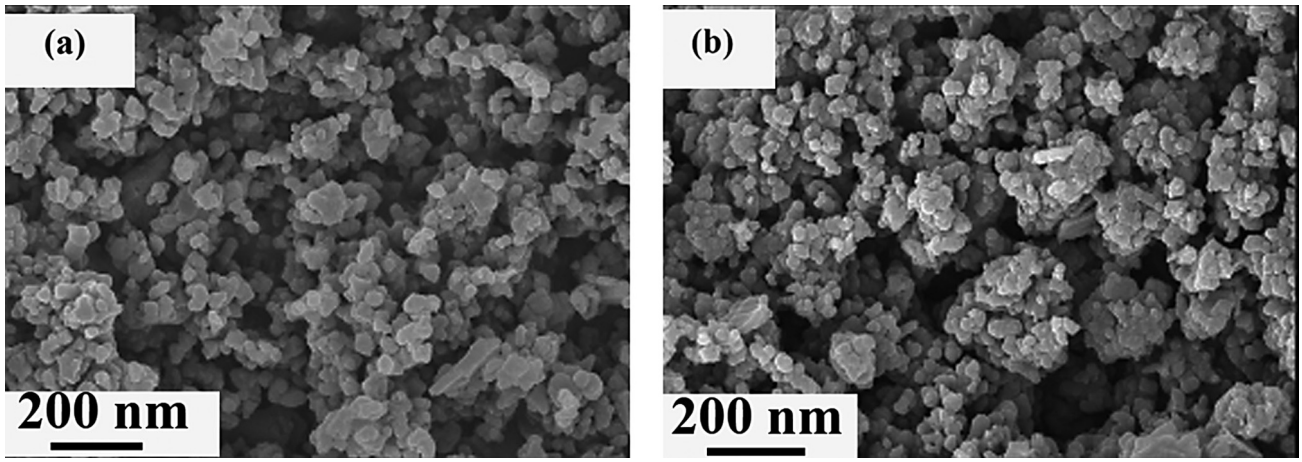

FIGURE 1.7 FESEM images of (a) polyindole and (b) polyindole/carbon black composite (Majumder et al. [39] with permission).

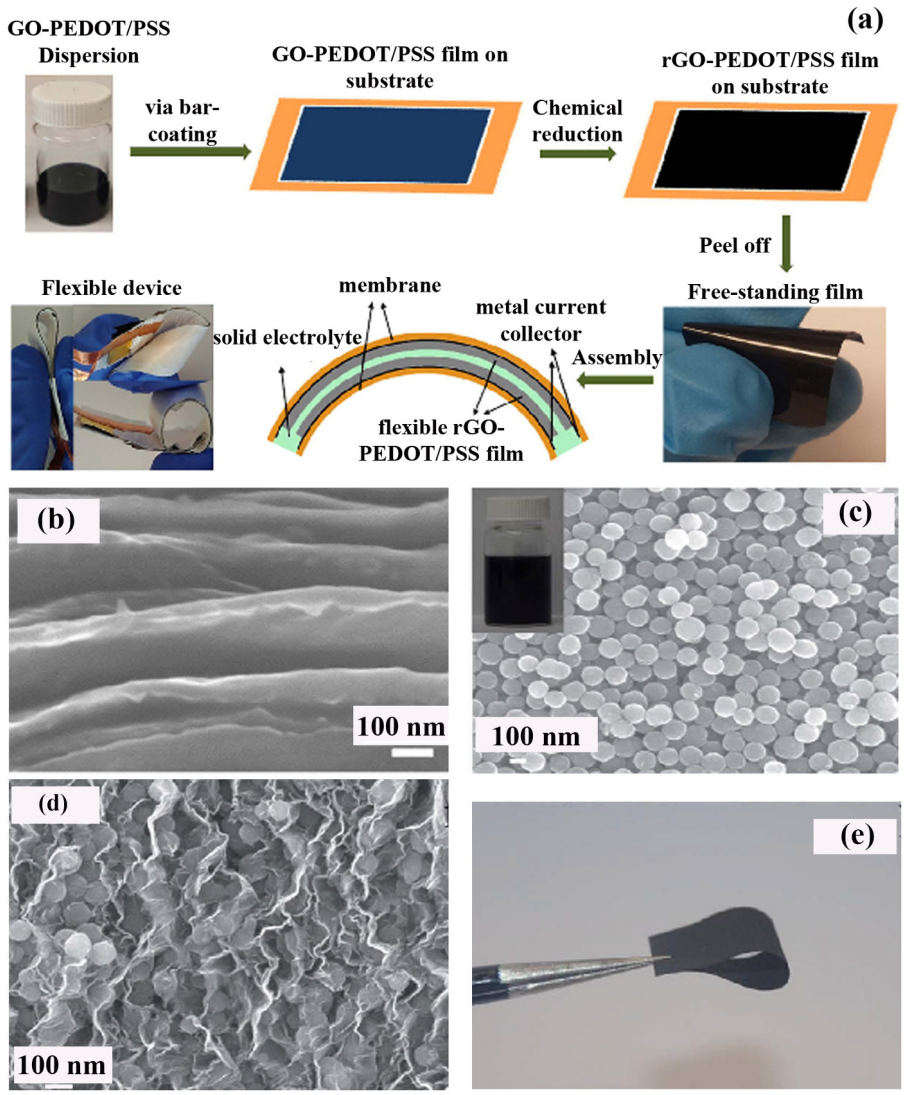

FIGURE 1.8 (a) A graphical illustration of rGO-PEDOT/PSS film preparation and assembled supercapacitor device structure. (b) rGO-PEDOT/PSS film scanning electron microscopy (SEM) cross-section image. SEM images for (c) PPy NPs (the inset is a PPy NPs aqueous dispersion image at 0.5 mg mL^{-1}), and (d) PPy/graphene film. (e) Image of a flexible PPy/graphene film (Ge et al. [40] with permission.

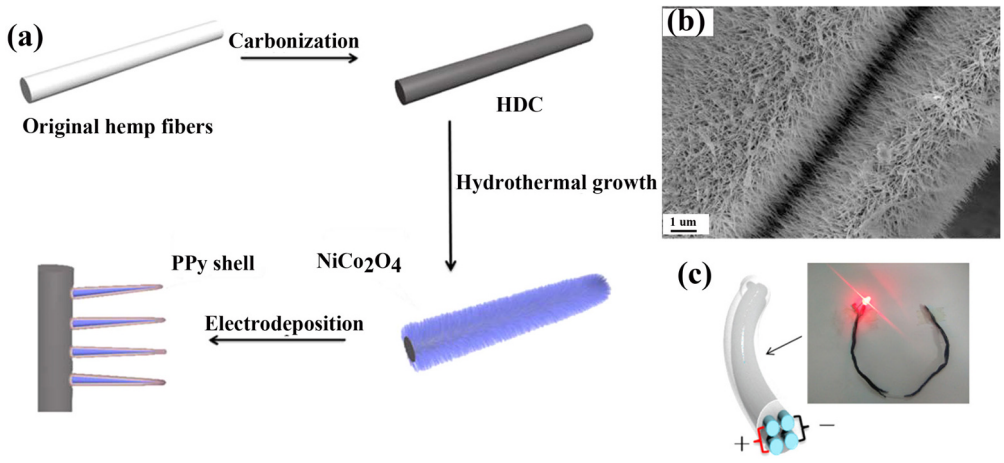

FIGURE 1.9 (a) Schematic representation of the preparation process of HDC@$NiCo_2O_4$@polypyrrole. (b) SEM image of the HDC@$NiCo_2O_4$ composite. (c) Schematic design of symmetric supercapacitor (the inset is a red LED powered by two supercapacitors connected in series).

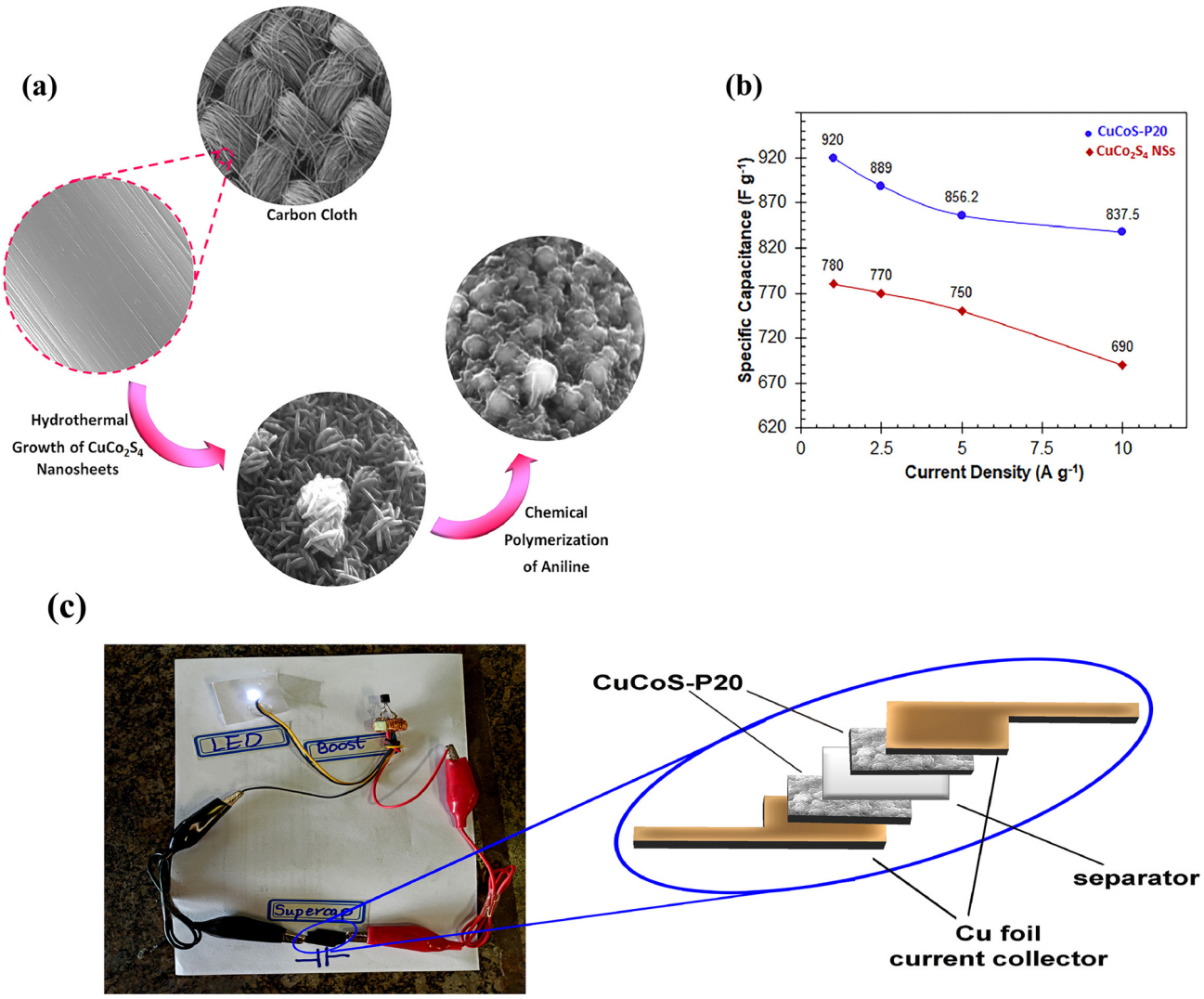

FIGURE 1.10 (a) Synthesis scheme of $CuCo_2S_4$ on carbon cloth and subsequent aniline polymerization. (b) Specific capacitances for pure and composite electrodes. (c) A fabricated device and schematic illustration of a symmetric supercapacitor assembled with $CuCo_2S_4$/polyaniline. Abuali et al. [43] with permission.

of the pure $CuCo_2S_4$ electrode and the $CuCo_2S_4$/polyaniline electrode was 88.46 and 91.03%, respectively, from 1 to 10 A g^{-1} (Figure 1.10b). This indicates that after composing with polyaniline, the rate capability of the $CuCo_2S_4$ electrode was improved, and the prepared nanocomposite performed better during rapid charge transfer. Such notable electrochemical performance was attributed to the enhancement of electrical conductivity rendered by the excellent coupling between $CuCo_2S_4$ and polyaniline.

In a 1 M Na_2SO_4 electrolyte, the $CuCo_2S_4$/polyaniline composite was used to assemble a symmetric supercapacitor. Figure 1.10c shows that the completely charged (1.8 V) device has been connected with the DC converter and can light up a 3.2 V white LED for a period of 12 min.

1.3 POLYMER MATERIALS FOR ENERGY CONVERSION APPLICATIONS

High efficient energy conversion systems such as fuel cells and solar cells can convert chemical to electrical energy. During the last decade, they have been actively developed. Considerable research has been undertaken on fuel cells such as the direct fuel cell of methanol, the polymeric electrolyte membrane fuel cell, the proton membrane exchange cell, and the alkaline cell. Due to the excellent conductivity and high flexibility of conducting polymers, which typically display high catalytic activity and good stability, they promise use as electrocatalysts of fuel cells. Several studies have shown that PANI-based electrocatalysts provide excellent catalytic activity in hydrogen evolution (HER), hydrogen oxidation (HOR), oxygen reduction (ORR), and methanol oxidation reaction (MOR). This section summarizes the recent research on metal electrocatalysts supported by PANI and metal-free electrocatalysts derived by PANI.

In 2011, Yuan et al. created an effective ORR electrocatalyst from a PANI/carbon black composite assisted iron phthalocyanine (PANI/FePc/C composite) for ORR in an air-cathode microbial fuel cell [44]. The resulting catalyst outperformed on bare Pt, PANI/C, and FePc/C in terms of catalytic activity, indicating that the activity of C in ORR is

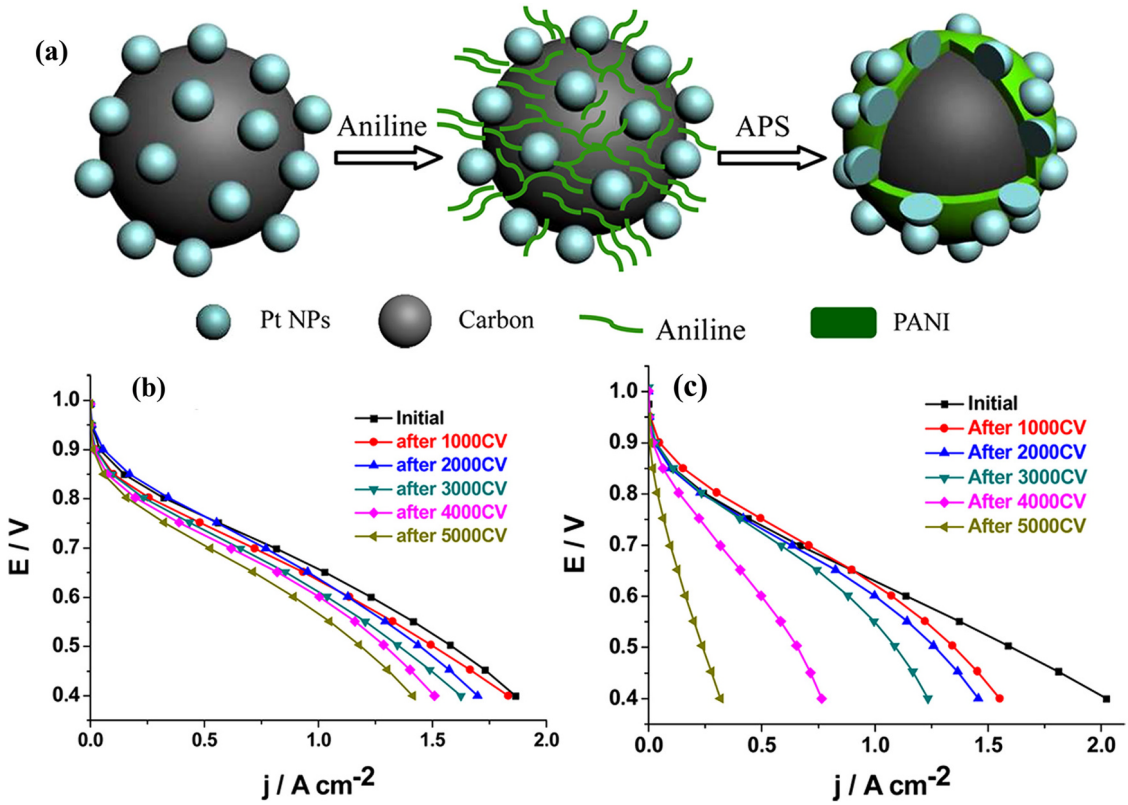

FIGURE 1.11 (a) Pt/C@PANI catalyst preparation process. Polarizing curves of single PEM cell fuel cells with (b) PANI@Pt/C (30%) and (c) Pt/C catalysts, following the indicated CV cycle numbers (Chen et al. [45] with permission).

improved by the PANI addition. Furthermore, a PANI/C/FePc catalyst had a power per cost that was much higher than the bare Pt catalyst. Chen et al. developed a PANI-decorated Pt/C@PANI core–shell catalyst in 2012, as shown in Figure 1.11a, with a 5 nm thickness PANI layer covering the Pt/C catalyst surface [45]. This core–shell structure caused electron delocalization between Pt and PANI-conjugated ligand d-orbitals, facilitating the electron transfer to PANI. As a result, it outperformed nondecorated Pt/C catalysts in terms of catalytic activity and durability (Figure 1.11b and c).

Zhang et al. prepared an MoS_2/PANI 3D catalyst, which achieved catalytic functionality with HER [46]. The flexible PANI inhibits MoS_2 aggregation, confirming that PANI branches with MoS_2 nanosheets are uniformly and vertically dispersed. In addition to other HER electrocatalysts based on polymer-MoS_2, the as-prepared MoS_2/PANI has achieved excellent stability.

Osmieri and co-workers used pyrrole to synthesize N-doped carbon-based material for ORR using a pyrolysis method with iron and cobalt salts [47]. In alkaline conditions, an excellent ORR activity, excellent surface stability, and well-developed current-restraint diffusion was achieved. The use of a 3D macroporous graphene/PANI anode in microbial fuel cells has been investigated [48]. SEM was used to verify the active deposition of PANI on the graphene surface by *in situ* polymerization (Figure 1.12a). The output of the as-prepared anode was compared to that of commercially available carbon cloth.

Bacteria attached to the graphene surface went deep within the 3D graphene/PANI (Figure 1.12b). The overall power density achieved from this microbial fuel cell (3D graphene/PANI) was 768 mW m^{-2} (four times higher than obtained from the carbon cloth microbial fuel cell (158 mW m^{-2})) [48]. Therefore, the 3D graphene/PANI electrode is a good candidate for high-performance and efficient microbial fuel cells. Yousfi et al. suggested a physical model for the analysis in a GO/poly (3-hexylthiophene) (P3HT) nanocomposite transistor thin film of portable concentration and mobility parameters as shown in Figure 1.13 [49]. This model has produced excellent results and has explained that the P3HT increase in the nanocomposite changed the interspace of the GO by the oxygen groups, which altered the energy of its bandgap.

By combining CdS/CdSe quantum dots with a P3HT/PCBM bulk heterojunction, Grissom et al. created flexible 3D CNT-based dye-sensitized solar cells [50]. The cells had good morphological properties and a high photon conversion rate of 7.6%. The cells are well-suited for extended multi-cell systems as they are performed in series and parallel configurations. As shown by the study findings, these novel three-dimensional optoelectronic-electrodes, which are low cost and innovative, have stable photovoltaic (PV) performance when enhanced by specific hybridization with

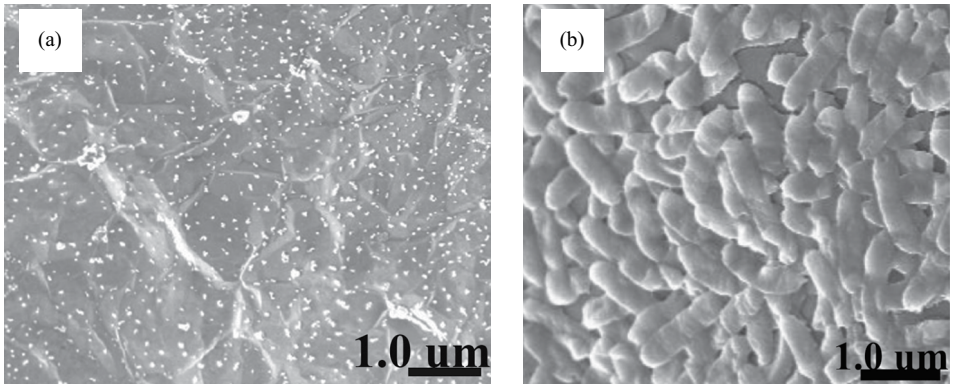

FIGURE 1.12 SEM images of (a) PANI/graphene composite and (b) bacteria cells on graphene/PANI surface. Yong et al. [48] with permission.

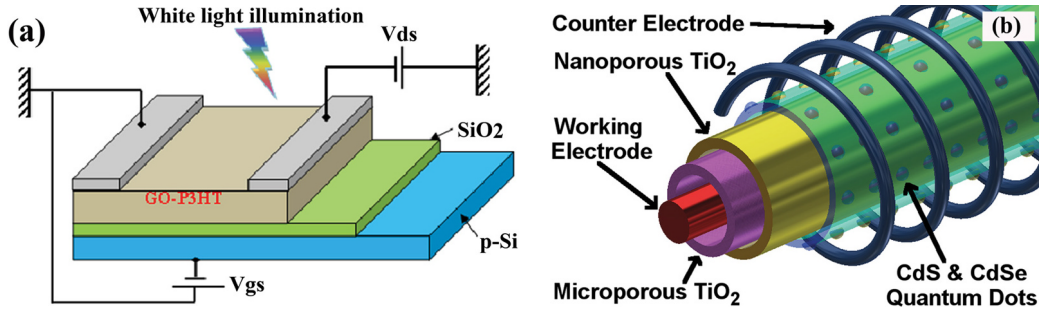

FIGURE 1.13 (a) GO/P3HT nanocomposite transistor scheme. (b) The structure of the photovoltaic cell. Yousfi et al. [49] with permission.

P3HT-PCBM. The hybrid interface formed by the inorganic CdS–CdSe QD layer and the organic P3HT-PCBM layer prevents the interfacial recombination of the photoinjected electrons from TiO_2 into the electrolyte from occurring.

1.4 CONCLUSION

Polymer materials have been used in various energy applications, including supercapacitors, batteries, solar cells, fuel cells, and electrochromic devices. Conducting polymers play an important role in electronic device fabrication. Carbon-based materials inserted into conducting polymers play a critical role in improving overall electrochemical efficiency. The electrodes' basic capacitance and cycling stability are enhanced synergistically for efficient energy storage applications by integrating both materials.

REFERENCES

1. Shi, L., Guo, Y., Hu, W., and Liu, Y. 2017. Design and effective synthesis methods for high-performance polymer semiconductors in organic field-effect transistors. *Materials Chemistry Frontiers* 1(12): 2423–2456.
2. Meng, Q., Cai, K., Chen, Y., and Chen, L. 2017. Research progress on conducting polymer based supercapacitor electrode materials. *Nano Energy* 36: 268–285.
3. Low, J.Y., Aljunid Merican, Z.M., and Hamza, M.F. 2019. Polymer light emitting diodes (PLEDs): An update review on current innovation and performance of material properties. *Materials Today: Proceedings* 16: 1909–1918.
4. Han, Y., and Dai, L. 2019. Conducting polymers for flexible supercapacitors. *Macromolecular Chemistry and Physics* 220(3): 1–14.
5. Hou, W., Xiao, Y., Han, G., and Lin, J.Y. 2019. The applications of polymers in solar cells: A review. *Polymers* 11(1): 1–46.
6. Chandran, P., Ghosh, A., and Ramaprabhu, S. 2018. High-performance platinum-free oxygen reduction reaction and hydrogen oxidation reaction catalyst in polymer electrolyte membrane fuel cell. *Scientific Reports* 8(1): 1–11.
7. Wisniak, J. 2000. Jöns Jacob Berzelius a guide to the perplexed chemist. *The Chemical Educator* 5(6): 343–350.
8. Feldman, D. 2008. Polymer history. *Designed Monomers and Polymers* 11(1): 1–15.
9. Frey, H., and Johann, T. 2019. Celebrating 100 years of "polymer science": Hermann Staudinger's 1920 manifesto. *Polymer Chemistry* 11(1): 8–14.
10. Ismail, N.H., and Mustapha, M. 2018. A review of thermoplastic elastomeric nanocomposites for high voltage insulation applications. *Polymer Engineering and Science* 58: E36–E63.
11. Shirakawa, H., Louis, E.J., MacDiarmid, A.G., Chiang, C.K., and Heeger, A.J. 1977. Synthesis of electrically conducting organic polymers: Halogen derivatives of polyacetylene, (CH)x. *Journal of the Chemical Society, Chemical Communications* (16): 578–580.
12. Tajik, S., Beitollahi, H., Nejad, F.G., Shoaie, I.S., Khalilzadeh, M.A., Asl, M.S., Van Le, Q., Zhang, K., Jang, H.W., and Shokouhimehr, M. 2020. Recent developments in conducting polymers: Applications for electrochemistry. *RSC Advances* 10(62): 37834–37856

13. Ali, G.A.M., Megiel, E., Cieciórski, P., Thalji, M.R., Romański, J., Algarni, H., and Chong, K.F. 2020. Ferrocene functionalized multi-walled carbon nanotubes as supercapacitor electrodes. *Journal of Molecular Liquids* 318: 114064.
14. Ali, G.A.M., Habeeb, O.A., Algarni, H., and Chong, K.F. 2019. CaO impregnated highly porous honeycomb activated carbon from agriculture waste: symmetrical supercapacitor study. *Journal of Materials Science* 54(1): 683–692.
15. Ali, G.A.M., Yusoff, M.M., Algarni, H., and Chong, K.F. 2018. One-step electrosynthesis of MnO_2/rGO nanocomposite and its enhanced electrochemical performance. *Ceramics International* 44(7): 7799–7807.
16. Thalji, M.R., Ali, G.A.M., Algarni, H., and Chong, K.F. 2019. Al^{3+} ion intercalation pseudocapacitance study of $W_{18}O_{49}$ nanostructure. *Journal of Power Sources* 438: 227028.
17. Han, X., Lu, L., Zheng, Y., Feng, X., Li, Z., Li, J., and Ouyang, M. 2019. A review on the key issues of the lithium ion battery degradation among the whole life cycle. *eTransportation* 1: 100005.
18. Ali, G.A.M. 2020. Recycled MnO_2 nanoflowers and graphene nanosheets for low-cost and high performance asymmetric supercapacitor. *Journal of Electronic Materials* 49(9): 5411–5421.
19. Thalji, M.R., Ali, G.A.M., Poh, S., and Chong, K.F. 2019. Solvothermal synthesis of reduced graphene oxide as electrode material for supercapacitor application. *Chemistry of Advanced Materials* 4(3): 17–26.
20. Ali, G.A.M., Fouad, O.A., Makhlouf, S.A., Yusoff, M.M., and Chong, K.F. 2014. Co_3O_4/SiO_2 nanocomposites for supercapacitor application. *Journal of Solid State Electrochemistry* 18(9): 2505–2512.
21. Ali, G.A.M., Yusoff, M.M., Shaaban, E.R., and Chong, K.F. 2017. High performance MnO_2 nanoflower supercapacitor electrode by electrochemical recycling of spent batteries. *Ceramics International* 43(11): 8440–8448.
22. Collins, J., Gourdin, G., Foster, M., and Qu, D. 2015. Carbon surface functionalities and SEI formation during Li intercalation. *Carbon* 92: 193–244.
23. Abbas, Q., Raza, R., Shabbir, I., and Olabi, A.G. 2019. Heteroatom doped high porosity carbon nanomaterials as electrodes for energy storage in electrochemical capacitors: A review. *Journal of Science: Advanced Materials and Devices* 4(3): 341–352
24. Vijayakumar, M., Santhosh, R., Adduru, J., Rao, T.N., and Karthik, M. 2018. Activated carbon fibres as high performance supercapacitor electrodes with commercial level mass loading. *Carbon* 140: 465–476.
25. Thalji, M.R., Ali, G.A.M., Liu, P., Zhong, Y.L., and Chong, K.F. 2021. $W_{18}O_{49}$ nanowires-graphene nanocomposite for asymmetric supercapacitors employing $AlCl_3$ aqueous electrolyte. *Chemical Engineering Journal* 409: 128216.
26. He, S., Wang, S., Chen, H., Hou, X., and Shao, Z. 2020. A new dual-ion hybrid energy storage system with energy density comparable to that of ternary lithium ion batteries. *Journal of Materials Chemistry A* 8(5): 2571–2580.
27. Ali, G.A.M., Thalji, M.R., Soh, W.C., Algarni, H., and Chong, K.F. 2020. One-step electrochemical synthesis of MoS_2/graphene composite for supercapacitor application. *Journal of Solid State Electrochemistry* 24(1): 25–34.
28. Aboelazm, E.A.A., Ali, G.A.M., Algarni, H., and Chong, K.F. 2018. Flakes size-dependent optical and electrochemical properties of MoS_2. *Current Nanoscience* 14(2): 1–5.
29. Da-Wei, W., Feng, L., Jinping, Z., Wencai, R., Zhi-Gang, C., Jun, T., Zhong-Shuai, W., Ian, G., Gao Qing, L., and Hui-Ming, C. 2009. Fabrication of graphene/polyaniline composite paper via in situ anodic electropolymerization for high-performance flexible electrode. *ACS Nano* 3(7): 1745–1752.
30. Feng, H., Wang, B., Tan, L., Chen, N., Wang, N., and Chen, B. 2014. Polypyrrole/hexadecylpyridinium chloride-modified graphite oxide composites: Fabrication, characterization, and application in supercapacitors. *Journal of Power Sources* 246: 621–628.
31. Ali, G.A.M., Yusoff, M.M., Ng, Y.H., Lim, N.H., and Chong, K.F. 2015. Potentiostatic and galvanostatic electrodeposition of MnO_2 for supercapacitors application: A comparison study. *Current Applied Physics* 15(10): 1143–1147.
32. Ali, G.A.M., Wahba, O.A.G., Hassan, A.M., Fouad, O.A., and Chong, K.F. 2015. Calcium-based nanosized mixed metal oxides for supercapacitor application. *Ceramics International* 41(6): 8230–8234.
33. Kim, J., Kim, J.H., and Ariga, K. 2017. Redox-active polymers for energy storage nanoarchitectonics. *Joule* 1(4): 739–768.
34. Shehata, N., Sayed, E.T., Abdelkareem, M.A., Ali, G.A.M., and Olabi, A.G. 2021. Smart Electronic Materials, in *Reference Module in Materials Science and Materials Engineering*, Elsevier.
35. Fusalba, F., Gouérec, P., Villers, D., and Bélanger, D. 2001. Electrochemical characterization of polyaniline in nonaqueous electrolyte and its evaluation as electrode material for electrochemical supercapacitors. *Journal of The Electrochemical Society* 148(1): A1.
36. Zhou, H., Chen, H., Luo, S., Lu, G., Wei, W., and Kuang, Y. 2005. The effect of the polyaniline morphology on the performance of polyaniline supercapacitors. *Journal of Solid State Electrochemistry* 9(8): 574–580.
37. Liu, J., Zhou, M., Fan, L.Z., Li, P., and Qu, X. 2010. Porous polyaniline exhibits highly enhanced electrochemical capacitance performance. *Electrochimica Acta* 55(20): 5819–5822.
38. Zhang, X., Zhao, J., Xia, T., Li, Q., Ao, C., Wang, Q., Zhang, W., Lu, C., and Deng, Y. 2020. Hollow polypyrrole/cellulose hydrogels for high-performance flexible supercapacitors. *Energy Storage Materials* 31: 135–145.
39. Majumder, M., Bilash, R., Koiry, S.P., and Thakur, A.K. 2017. Gravimetric and volumetric capacitive performance of polyindole/carbon black/MoS_2 hybrid electrode material for supercapacitor applications. *Electrochimica Acta* 248: 98–111.
40. Ge, Y., Wang, C., Shu, K., Zhao, C., Jia, X., Gambhir, S., and Wallace, G.G. 2015. A facile approach for fabrication of mechanically strong graphene/polypyrrole films with large areal capacitance for supercapacitor applications. *RSC Advances* 5(124): 102643–102651.
41. Liu, Y., Weng, B., Razal, J.M., Xu, Q., Zhao, C., Hou, Y., Seyedin, S., Jalili, R., Wallace, G.G., and Chen, J. 2015. High-performance flexible all-solid-state supercapacitor from large free-standing graphene-PEDOT/PSS films. *Scientific Reports* 5: 1–11.
42. Xiong, W., Hu, X., Wu, X., Zeng, Y., Wang, B., He, G., and Zhu, Z. 2015. A flexible fiber-shaped supercapacitor utilizing hierarchical $NiCo_2O_4$@polypyrrole core-shell nanowires on hemp-derived carbon. *Journal of Materials Chemistry A* 3(33): 17209–17216
43. Abuali, M., Arsalani, N., and Ahadzadeh, I. 2020. Investigation of electrochemical performance of a new nanocomposite: $CuCo_2S_4$/polyaniline on carbon cloth. *Journal of Energy Storage* 32: 101694–101694.

44. Yuan, Y., Ahmed, J., and Kim, S. 2011. Polyaniline/carbon black composite-supported iron phthalocyanine as an oxygen reduction catalyst for microbial fuel cells. *Journal of Power Sources* 196(3): 1103–1106.
45. Chen, Siguo, Wei, Zidong, Qi, XueQiang, Dong, Lichun, Guo, Yu-Guo, Wan, Lijun, Shao, Zhigang, and Li, L. 2012. Nanostructured polyaniline-decorated Pt/C@PANI core–shell catalyst with enhanced durability and activity. *Journal of the American Chemical Society* 134: 13252–13255.
46. Zhang, N., Ma, W., Wu, T., Wang, H., Han, D., and Niu, L. 2015. Electrochimica acta edge-rich MoS_2 naonosheets rooting into polyaniline nano fi bers as effective catalyst for electrochemical hydrogen evolution. *Electrochimica Acta* 180: 155–163.
47. Osmieri, A.L., Zafferoni, C., Wang, L., Videla, H.A.M., and Lavacchi, A. 2018. Polypyrrole-derived Fe-Co-N-C catalyst for oxygen reduction reaction: Performance in alkaline hydrogen and ethanol fuel cells. *ChemElectroChem* 5(14): 1954–1965.
48. Yong, Y.C., Dong, X.C., Chan-Park, M.B., Song, H., and Chen, P. 2012. Macroporous and monolithic anode based on polyaniline hybridized three-dimensional Graphene for high-performance microbial fuel cells. *ACS Nano* 6(3): 2394–2400.
49. Yousfi, Y., Jouili, A., Mansouri, S., El Mir, L., Al-Ghamdi, A., and Yakuphanoglu, F. 2020. Studies of the dirac point in a GO/P3HT nanocomposite thin-film phototransistor. *Journal of Electronic Materials* 49(10): 5808–5815.
50. Grissom, G., Jaksik, J., McEntee, M., Durke, E.M., Aishee, S.T.J., Cua, M., Okoli, O., Touhami, A., Moore, H.J., and Uddin, M.J. 2018. Three-dimensional carbon nanotube yarn based solid state solar cells with multiple sensitizers exhibit high energy conversion efficiency. *Solar Energy* 171: 16–22.