

Feng Wang, Yaqin Huang, and Jin Niu

# Collagen-Derived Materials

Synthesis and Applications in  
Electrochemical Energy Storage and Conversion





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Synthesis and Applications in Electrochemical Energy  
Storage and Conversion

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**WILEY-VCH**

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## Preface

Global energy demand and environmental degradation have resulted in a severe crisis in the sustainable development of the international community. In this context, it is necessary to develop high-efficiency electrochemical energy storage and conversion devices to address the challenges. The assembly of the devices needs materials (especially electrode materials) that should not only show high performance but also have sustainability and low cost.

As one kind of natural biomass, collagen exists in the connective tissues of animals, comprising 23 kinds of amino acids. As the hydrolysate of collagen, gelatin has unique water solubility, rheological property, and gel property. By virtue of rich carbon atoms and non-carbon atoms (e.g. nitrogen, oxygen, and sulfur), collagen and gelatin can be converted into a new kind of carbon material. The collagen-derived carbons have heteroatom doping and unique morphologies, which are derived from the natural structural compositions of the collagen-enriched precursors. By virtue of their structural compositions and unique properties, the collagen-derived materials (including gelatin and collagen-derived carbons) show promising applications in electrochemical energy storage and conversion.

Our group has been devoted to collagen and collagen-derived materials since 1997. We started from the gelatin extraction from collagen and gradually expanded the applications of collagen-derived materials. So far, gelatin with and without modification has been used as different modifying agents for electrodes, separators, and electrolytes. Collagen-derived carbons with different morphology structures and chemical compositions have also been used as electrodes and support materials for electrochemical energy storage and conversion. Based on the related works, we have published over 100 peer-reviewed journal papers and authored more than 40 patents.

This book is based on our published works and also includes typical works by other researchers. It is divided into ten chapters, and written by Prof. Feng Wang, Prof. Yaqin Huang, and Prof. Jin Niu. This book covers basic knowledge of collagen and collagen-derived materials, and their typical synthesis and applications. Moreover, it also presents the up-to-date ideas and strategies for the synthesis and characterization of advanced collagen-derived materials, as well as multifunctional applications in electrochemical energy storage and conversion. Therefore, this book can not only enable students and new researchers to obtain easy understanding of these materials

and their applications but also serve as an important reference book for scientists and engineers in other research fields.

I would like to thank the other group members for their assistance during the book writing, including Mengyue Liu, Yongzheng Shi, Feng Zhu, Junhui Sun, Binke Li, Na Yang, Rong Shao, Jiaying Liu, and Weihao Song. I would also like to thank my current and former group members, as well as collaborators who have contributed to the study on collagen-derived materials. Finally, we would like to acknowledge the financial support from the National Natural Science Foundation of China (52130206, U20A20337, 51432003, 22178016, and 52003025) and Fundamental Research Funds for the Central Universities (buctrc202024).

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10 August 2021

*Feng Wang*

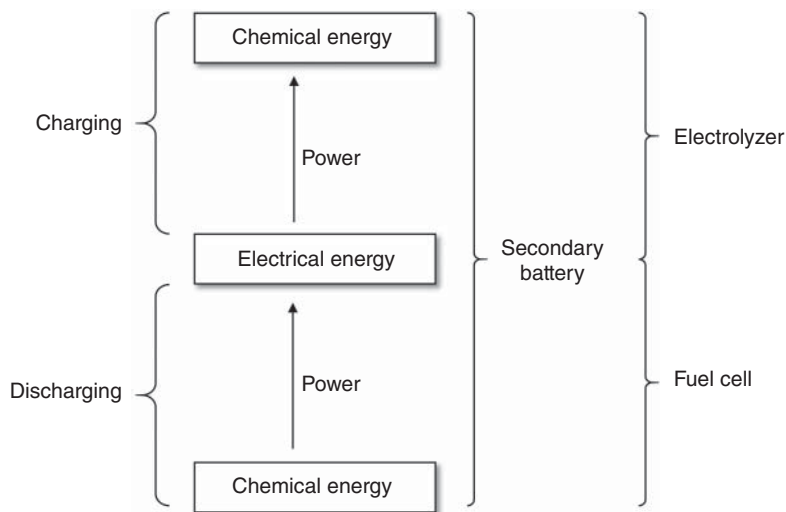
# 1

## Introduction

### 1.1 Electrochemical Energy Storage and Conversion

Electric energy plays a very important role in our daily life and industrial production. Fossil fuel, nuclear heat, and renewable energies (e.g. solar energy, wind energy, and biomass energy) all can be converted into electric energy [1]. Unfortunately, the energy-conversion processes are always accompanied by a lot of energy loss. For instance, the conversion efficiency of nuclear heat to electric energy is only ~30%. Moreover, the electric energy derived from renewable energies depends highly on weather, season, and territory, which cannot meet the actual demand in time. Thus, it is an urgent need to address the issue of electric energy storage and conversion.

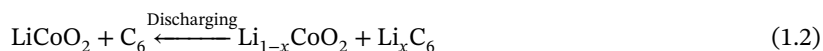
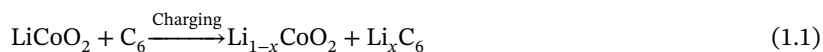
Developing advanced energy storage and conversion technologies is critical to improving the energy utilization efficiency and expanding the energy application field. Secondary batteries, supercapacitors, water electrolyzers, and fuel cells are some of the typical electrochemical energy storage and conversion devices. Figure 1.1 shows the schematics of these electrochemical energy storage and conversion systems [2]. Electric energy can be converted into chemical energy by water electrolyzers, producing hydrogen (with a conversion efficiency of ~70%) for further use in fuel cells. In the opposite process, fuel cells convert chemical energy into electric energy. The energy-conversion process is reversible in secondary batteries (e.g. lithium-ion battery). Electric energy can be converted into chemical energy in the charging process [3]. In the discharging process, the chemical energy is converted back into electric energy. The conversion speed determines the system power, while the storage capacity is relevant to the system energy. Generally, the active materials for energy conversion and storage are integrated into secondary batteries because of the internal system. Different from secondary batteries, the electrolyzer and fuel cell systems are suitable for separated converters and storage. This kind of electrochemical storage and conversion systems commonly supplies higher energy than that with integrated storage and converters. Therefore, electrolyzers and fuel cells have also attracted much attention [4]. Herein, a brief overview of typical secondary batteries, supercapacitors, fuel cells, and water electrolyzers is presented.



**Figure 1.1** Schematics of typical systems for electrochemical energy storage and conversion. Source: Modified from Shen et al. [2]; © 2016, Taylor & Francis Group.

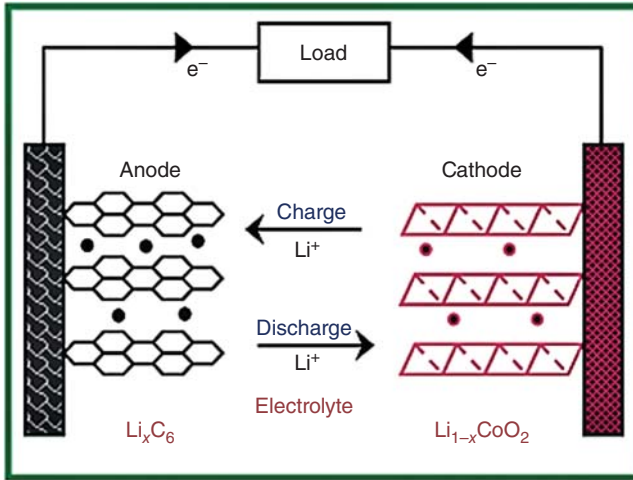
### 1.1.1 Secondary Batteries and Supercapacitors

Currently, secondary batteries and supercapacitors are regarded as the most efficient electrochemical systems for electric energy storage and conversion. As a typical secondary battery, lithium-ion battery has been widely studied and commercialized. The working mechanism of lithium-ion battery is shown in Figure 1.2. It involves a reversible intercalation/deintercalation of Li ions into/from host materials, combined with electron flow through the external circuit in the charging/discharging process [5]. Taking a commercial lithium-ion battery as an example, graphite and layered  $\text{LiCoO}_2$  are usually employed as anode host and cathode host, respectively. A mixture of lithium-containing salt (e.g.  $\text{LiPF}_6$ ) and organic solvents (e.g. diethyl carbonate and ethylene carbonate) is commonly used as an electrolyte. The chemical reactions during the charging and discharging process are shown as below:

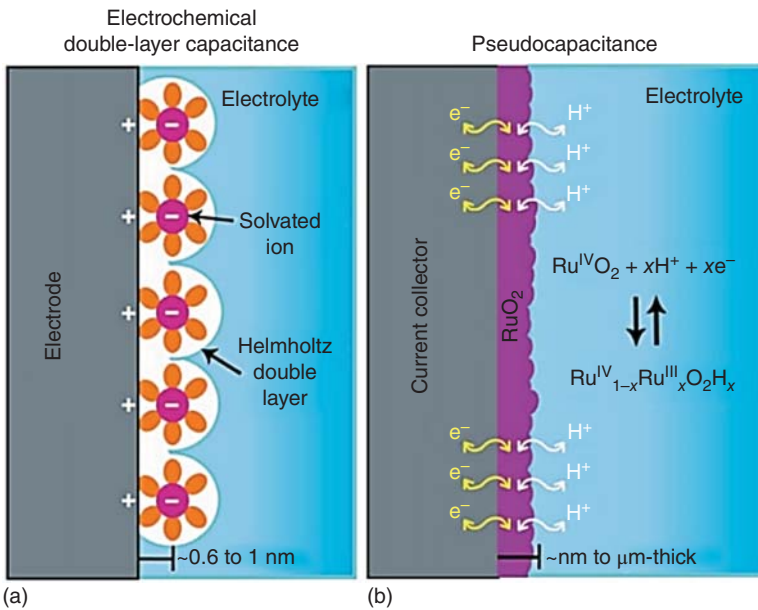


As a “rocking chair” battery, the energy storage and release of the lithium-ion battery primarily depend on the “rock” of Li ions between cathode and anode. As compared with Ni-based battery and lead–acid battery, the lithium-ion battery possesses characteristics of higher energy density and longer lifetime. Moreover, the lithium-ion battery is easier to be integrated into portable devices.

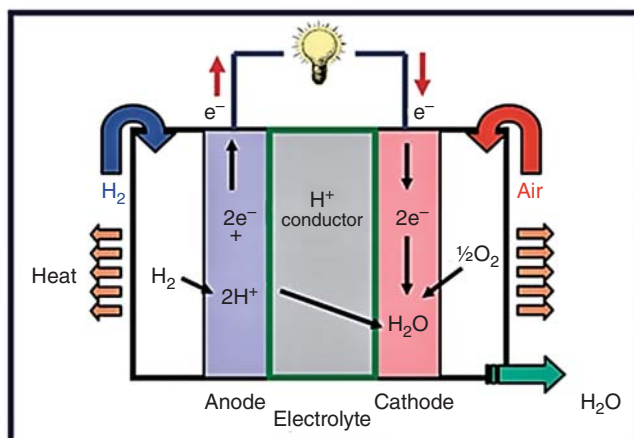
Based on the energy storage mechanisms, supercapacitors are primarily classified into electric double-layer capacitors (EDLCs) and pseudocapacitors (Figure 1.3) [7]. No matter what kind of mechanism, the charge storage occurs only on the electrode surface without ion diffusion within the electrode bulk, which endows



**Figure 1.2** Illustration of the charging/discharging process within a lithium-ion battery, composed of a graphite anode and a  $\text{LiCoO}_2$  cathode. Source: Reproduced with permission from Manthiram et al. [5]; © 2008, The Royal Society of Chemistry.



**Figure 1.3** Schematic of energy storage mechanisms of (a) an EDLC and (b) a pseudocapacitor. Source: Reproduced with permission from Simon et al. [6]; © 2011, Materials Research Society.



**Figure 1.4** Schematic of a PEMFC. Source: Reproduced with permission from Manthiram et al. [5]; © 2008, The Royal Society of Chemistry.

supercapacitors with a higher power density ( $\sim 10 \text{ kW kg}^{-1}$ ) but lower energy density ( $< 10 \text{ Wh kg}^{-1}$ ) than lithium-ion battery [6]. The EDLC stores energy through the fast adsorption and desorption of electrolyte ions at the electrode/electrolyte interface, which forms the electric double layer during the charging/discharging process. The pseudocapacitor reversibly stores energy via Faradaic reactions or surface redox reactions, which also occur at the electrode surface [8].

### 1.1.2 Fuel Cells and Electrolyzers

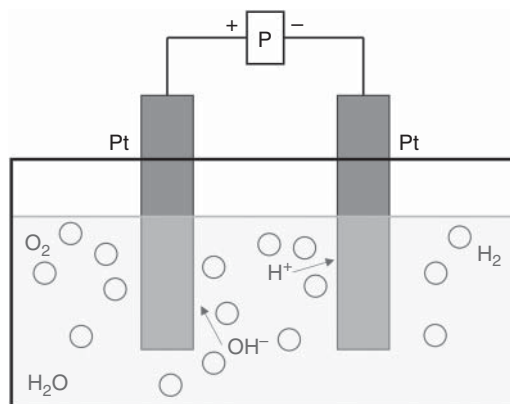
Fuel cells are promising energy-conversion devices because they can show high conversion efficiency besides being environment friendly. Among the different kinds of fuel cells, the proton exchange membrane fuel cell (PEMFC) is widely studied by virtue of its high energy delivery and low working temperature ( $< 100^\circ \text{C}$ ) [9, 10]. Figure 1.4 shows the working process of a PEMFC that uses oxygen and hydrogen as oxidant and fuel, respectively [5].  $\text{H}^+$  ions are generated through the electrocatalytic oxidation of  $\text{H}_2$  gas on the surface of an anode with Pt catalyst, which further migrates through a Nafion membrane with high proton conductivity. Meanwhile, the electrons move from anode to cathode through an external circuit and electrocatalytically reduce  $\text{O}_2$  gas to  $\text{O}^{2-}$  ions on the cathode surface with the assistance of Pt catalyst. Water is produced by the combination of the  $\text{H}^+$  and  $\text{O}^{2-}$  ions. Thus, the chemical energy involved in reaction 1.4 is converted into electricity:



Contrary to fuel cells, electrolyzers convert electric energy to chemical energy. Figure 1.5 displays a schematic representation of a water electrolyzer, which mainly consists of a cathode, an anode, an electrolyte, and an external power. At a critical voltage, electrons flow from the power source to the cathode and reduce  $\text{H}^+$  ions to  $\text{H}_2$  gas. At the same time,  $\text{OH}^-$  ions move to the anode through the electrolyte to



**Figure 1.5** Schematic of a water electrolyzer. Source: Reproduced with permission from Ma et al. [11]; © 2008, Elsevier Ltd.



keep an electrical charge balance.  $\text{O}_2$  gas is then generated by oxidization of  $\text{OH}^-$  ions by giving away electrons. Then, the electrons flow back to the power source. The half-reactions occurring on the electrodes are represented below:

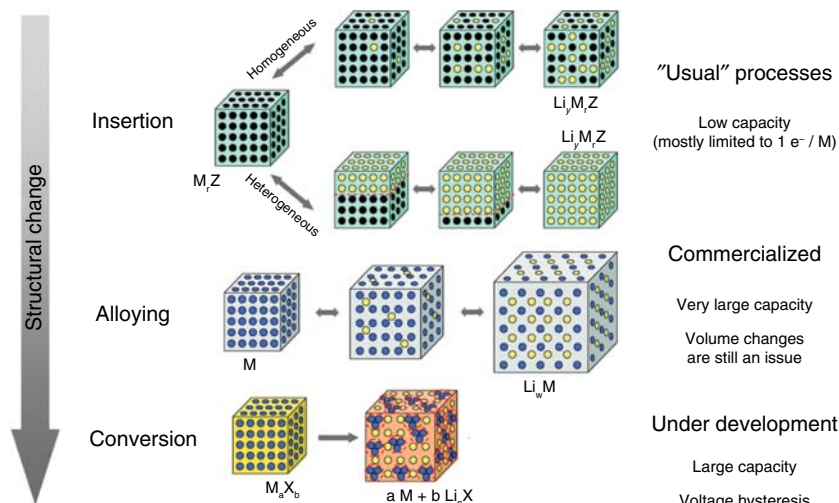


## 1.2 Materials for Electrochemical Energy Storage and Conversion

Materials (especially electrode materials) play very important roles in the performance of the aforementioned devices. Great efforts have been devoted to developing novel materials to improve the device's performance. Herein, we review typical materials for lithium-ion batteries, supercapacitors, and electrocatalysis (especially for oxygen reduction and evolution reactions).

### 1.2.1 Materials for Lithium-Ion Batteries

Based on the lithium-ion storage mechanism, the anode materials for the lithium-ion battery can be classified into intercalated-type materials (e.g. graphite, carbon nanotubes, and  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ), conversion-type materials (e.g.  $\text{SnO}_2$ ,  $\text{V}_2\text{O}_5$ , and  $\text{MoS}_2$ ), alloy-type materials (e.g. Si and Sn), and organic materials (e.g. carboxylates) [12] (Figure 1.6). To date, graphite is the most used anode material owing to its low cost, good thermal stability, and low working potential. Although conversion-type and alloy-type anode materials have a high theoretical capacity, they commonly have poor electrical conductivity and show large volume change during the lithiation process, which results in low coulombic efficiency and short lifetime in practical cells. Layered transition metal oxides are generally used as cathode materials for lithium-ion battery, such as  $\text{LiFePO}_4$ ,  $\text{LiCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$ , and  $\text{Li}[\text{Ni}_x\text{Co}_y\text{Mn}_z]\text{O}_2$  [13]. The electrolytes for lithium-ion battery are mainly composed of lithium-containing salt (e.g.  $\text{LiPF}_6$ ) and organic carbonate solvents



**Figure 1.6** Different types of anode materials for lithium-ion batteries. Source: Reproduced with permission from Long et al. [12]; © 2009, The Royal Society of Chemistry.

(e.g. ethylene carbonate), which are used for the balance of fluidity and dielectric constant. As separator, electronically insulated polymer film (e.g. polypropylene) with high porosity is widely used to avoid the direct contact between cathode and anode as well as ensure fast lithium-ion transport.

### 1.2.2 Materials for Supercapacitors

Carbon materials (e.g. activated carbons, graphene, carbon nanotubes, and porous carbons) have been employed as electrode materials for EDLC owing to their easy processing, large specific surface area, high electronic conductivity, and good chemical stability. Generally, the capacitance of EDLCs can be enlarged when the specific surface area of carbon electrode material is increased. In addition to the high specific surface area, suitable porosity for accessible ions (e.g. pore shape, pore size, and pore size distribution) also significantly influences the capacitance. For instance, the hierarchical porous structure can facilitate ion insertion and diffusion, thus endowing carbon electrodes with high capacitance and good rate capability. The electrode materials for pseudocapacitor contribute capacitance by reversible and rapid redox reactions, occurring on the electrode surface. Metal oxides (e.g.  $RuO_2$ ), metal carbides (e.g. MXene), electronically conducting polymers (e.g. polyaniline), and functionalized nanocarbons (e.g. heteroatom-doped graphene) are widely used as electrode materials for pseudocapacitor [6]. In addition, some biomaterials with functional groups (e.g. protein) are also electrode materials that can deliver pseudocapacitance [14]. The electrolytes for supercapacitors include aqueous and nonaqueous (including organic and ionic liquid) systems [15]. The two standards for choosing electrolytes are stable electrochemical window and high ionic conductivity, which determine the energy and power densities of the supercapacitors,

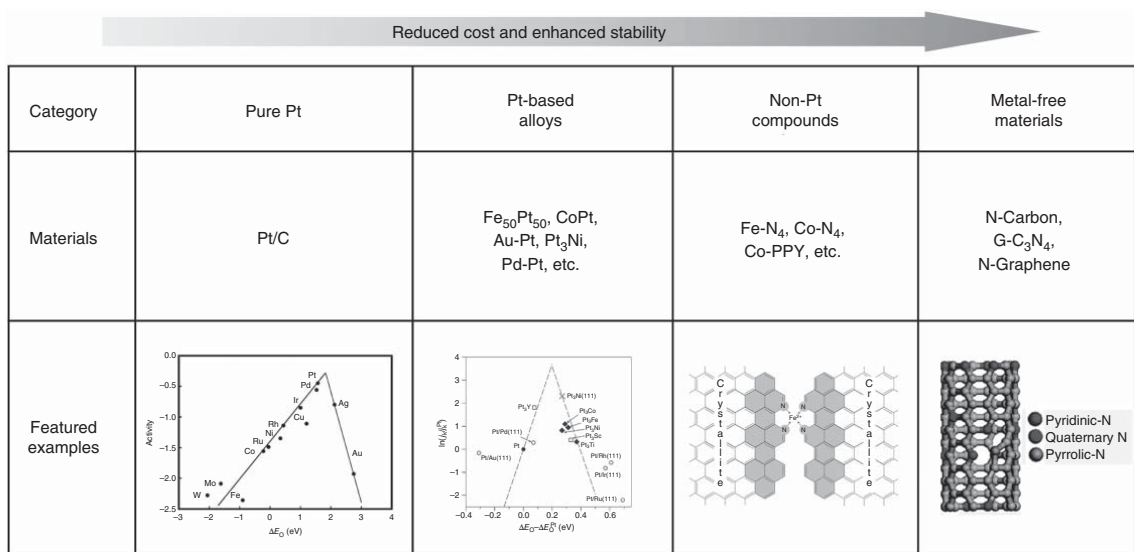
respectively. In comparison with organic electrolytes (with wide electrochemical windows ranging from 2.5 to 3.5 V), alkali- (e.g. KOH) and acid-based (e.g. H<sub>2</sub>SO<sub>4</sub>) aqueous electrolytes provide a higher ionic conductivity (up to  $\sim 1 \text{ S cm}^{-1}$ ) but a lower electrochemical window (1.0–1.8 V). Ionic liquid electrolytes show the widest electrochemical window (3.0–5.5 V) but the lowest ionic conductivity among these three electrolytes.

### 1.2.3 Materials for Oxygen Electrochemistry

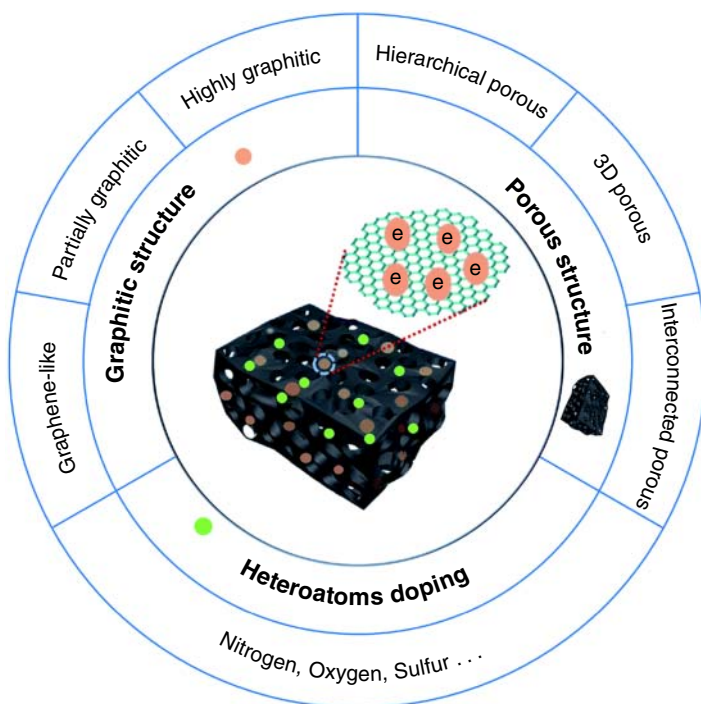
The performance of water electrolyzers and fuel cells is primarily restricted by oxygen reduction reactions (ORRs) and oxygen evolution reactions (OERs) performance [16]. Although oxygen is a kind of clean and abundant resource, its efficient and controllable use is difficult because the sluggish kinetic processes of ORR and OER lead to the low device efficiency in acidic and alkaline electrolytes [17]. The electrocatalysts for ORR and OER can be divided into precious metallic catalysts, non-noble metallic catalysts, and carbon-based catalysts (Figure 1.7). Pt catalyst has been used as an ORR electrocatalyst since the 1960s, and it is still widely studied because it not only shows a superior ORR performance but also provides a relatively simple system for investigating the ORR mechanism [19]. Pt-based alloy materials show more excellent ORR activity and stability than a pure Pt electrocatalyst. The selected secondary metals and the alloy architectures are of great importance to the performance of Pt-based alloy electrocatalysts. Non-noble metals (e.g. Ni-, Fe-, Co-, and Mn-based oxides) are the most promising candidates to Pt because of their better electrocatalysis activities in alkaline solutions [20, 21]. By virtue of low cost and high electric conductivity, carbon materials with heteroatom doping (e.g. nitrogen, oxygen, sulfur, phosphor, boron) have attracted extensive attention as electrocatalysts for ORR and OER. However, precious metallic catalysts and non-noble metallic catalysts generally show better activity and practical performance than carbon materials.

### 1.2.4 Biomass-Derived Materials for Electrochemical Energy Storage and Conversion

It is well established that the ever-increasing global energy demand and environmental degradation have resulted in a severe crisis in the sustainable development of the international community [22]. In this context, it is imperative to develop high-performance energy storage and conversion devices to address the challenges. The assembly of the devices needs materials (e.g. electrode materials) that should not only show high performance but also have sustainability and low cost. Biomass-derived materials are such kind of materials for the energy storage and conversion devices because of their excellent characteristics, which include: (i) As the most abundant carbon source in nature, biomass is derived from all life species (including animals, plants, and microorganisms); (ii) Biomass possesses inherently unique microarchitecture, which is beneficial for the design of microstructured materials (especially electrode materials). (iii) Some biomass also contains non-carbon elements (e.g. nitrogen, oxygen, sulfur, and phosphor). These



**Figure 1.7** Progress in the development of ORR electrochemical catalysts. Source: Reproduced with permission from Chen et al. [18]; © 2012, John Wiley & Sons.



**Figure 1.8** Schematic diagram showing the structure and properties of biomass-derived materials. Source: Reproduced with permission from Zheng et al. [23]; © 2020, The Royal Society of Chemistry.

heteroatoms can be in situ doped into biomass-derived carbons during the carbonization process, introducing additional active sites to enhance the performance of biomass-derived carbon electrodes. Therefore, biomass-derived materials have been widely prepared and used for electrochemical energy storage and conversion devices in recent years (Figure 1.8). Table 1.1 shows the properties and applications of the biomass-derived materials for different devices [3].

### 1.3 Collagen-Derived Materials for Electrochemical Energy Storage and Conversion

As one kind of natural fibrous protein, collagen exists in the connective tissue of animals. It is composed of 23 kinds of amino acids (mainly including glycine, proline, and alanine). Collagen consists of three polypeptide chains that assemble in a triple helix by hydrogen and hydrophobic bonds [24]. The polypeptide chains contain two identical chains ( $\alpha 1$ ) and an additional chain ( $\alpha 2$ ), which have slightly different chemical compositions. Figure 1.9 illustrates the hierarchical structure of a collagen triple helix. A single-collagen fiber is called tropocollagen, which has a diameter of  $\sim 1.6$  nm and a length of  $\sim 300$  nm. So far, 28 different types of collagen have been

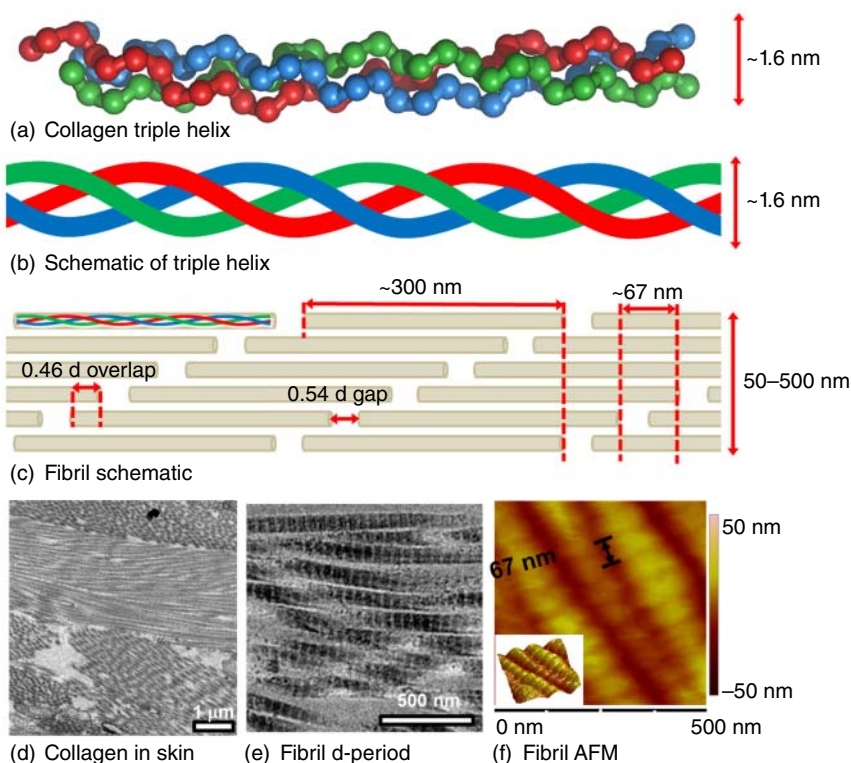
**Table 1.1** Biomass-derived materials for electrochemical energy storage and conversion [3].

Electrochemical energy storage and conversion devices	Roles of biomass-derived materials	Biomass-derived materials	Desired features of the biomass-derived materials
Supercapacitor	Electrode	Porous/activated carbon	Porous, conducting, high specific surface area, double-layer capacitance, functional groups, heteroatom doping, engineered pore structure
Lithium-ion battery	Anode electrode	Hard/soft carbon	Micrographite domain for Li/Na intercalation, conducting, porosity
PEMFC	Electrocatalyst or catalyst support	Porous/activated carbon	Conducting, high specific surface area, heteroatom doping catalytic property for ORR
PEMFC	Gas diffusion layer	Porous/activated carbon, carbon cloth/felt	Conducting, high porosity, hydrophobic
Lithium-ion battery; Supercapacitor	Electrode binder	Cellulose, chitosan, other polysaccharides	Polymer chain and binding ability, chemical stability, functional groups
Supercapacitor	Electrolyte	Organic acids and salts	Ion conductivity, stability over a reasonably wide potential window
Lithium-ion battery; supercapacitor	Separator	Cellulose, fiber	Electron insulator, thin film, wettability, flexibility, mechanical strength, chemical stability

Source: Yu et al. [3]/John Wiley & Sons.

discovered, which are divided into fibrillar and non-fibrillar collagen based on their structures [26].

As a soluble protein compound, gelatin is produced by partially hydrolyzing collagen within animals. During the hydrolysis process, three polypeptide chains are disentangled and the collagen molecules are dissociated into smaller molecules, after breaking the hydrogen bonds and hydrophobic bonds [27]. Thus, the structure, composition, and properties of gelatin are dependent on the collagen sources and types. It contains 18 kinds of amino acids. Different from collagen, gelatin consists of a relatively high content of nonpolar amino acids (>80%, such as glycine, proline,



**Figure 1.9** Overview of the hierarchical structure for collagen triple helix. (a, b) Schematic illustration of a collagen triple helix. (c) Schematic illustration of collagen fibrils. (d) Cross-section image of collagen fibrils in skin. (e) Transmission electron microscopy image of collagen fibrils. (f) Atomic force microscope image of collagen fibrils. Source: Sherman et al. [25]/with permission of © Elsevier Ltd.

and alanine). In addition to essential physicochemical characteristics (e.g. solubility, transparency, and color), gelatin has unique rheological property, gel strength, and thermal stability, which are mainly dependent on its molecular structures [28]. Since the polypeptide chains are composed of various amino acids with rich carbon, nitrogen, oxygen, and sulfur atoms, collagen and gelatin can be converted into carbon materials by controllable carbonization. The collagen-derived carbons have heteroatom doping and unique morphologies, which are derived from the structural compositions of collagen.

By virtue of their structures and compositions, the collagen-derived materials (including gelatin and collagen-derived carbons) show promising applications in electrochemical energy storage and conversion. Gelatin materials with and without modification have been used as various modifying agents for electrodes [29], separators [30], and electrolytes [31]. Collagen-derived carbons with different morphology structures and chemical compositions have also been prepared by different methods. They have been used as electrodes or support materials for electrochemical energy storage (e.g. supercapacitors [32], alkali-ion batteries [33],

and lithium–sulfur batteries [34]) and electrochemical energy conversion (e.g. oxygen reduction reactions [35], oxygen evolution reactions [36], and hydrogen evolution reactions [37]), showing good performance and practical prospect.

This book presents basic knowledge of collagen, collagen-derived materials, and their conventional synthesis and applications. Moreover, new strategies for the synthesis of advanced collagen-derived materials and their multifunctional applications in electrochemical energy storage and conversion are also summarized.

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## 2

# Collagen

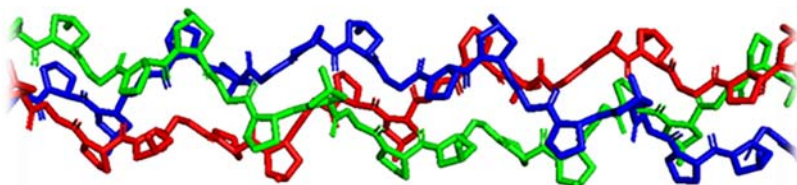
## 2.1 History of Collagen

The word “collagen” comes from Greek, which means “glue producer.” Collagen can be gradually hydrolyzed into water-soluble gelatin (also referred to as animal glue) when it is treated with hot water. As the richest protein in animals, collagen is the primary composition for the connective tissues and extracellular matrices. By virtue of its unique structure, collagen can form insoluble fibers that endow animal tissues with high strength [1].

In the 1950s, modern studies on collagen started, especially at a molecular level. As typical researchers and works, Highberger et al. [2] and Schmitt et al. [3] used an electron microscope to characterize the structure of collagen molecule. Then, Ramachandran and Kartha [4] and Rich and Crick [5] developed the triple-helical structure models of the collagen. Finally, Boedtger and Doty [6] measured the physical and chemical properties of the collagen in solution [7].

In the 1960s, detailed information about collagen and its structure was further revealed by Miller et al. through the investigation of protein chemistry and biochemistry [8, 9]. Based on the electron microscope results, it was found that band-shape-like collagen fibrils with a length of 70 nm are composed of three different but homologous collagen types, including types I, II, and III. Type I collagen is the most abundant among them; type II is the main collagenous component within cartilage; type III coexists with type I with different content in most tissues. After the discovery of type II and III collagen, Kefalides reported that a specific collagen is also present within basement membranes, which was categorized as the type IV collagen [10]. Then, Kuhn et al. [11] and Timpl et al. [12] showed that the structure of the type IV collagen is obviously different from that of the collagen, which can form fibers.

In addition to the above collagens, the type VI, VII, IX, and X collagens were also reported subsequently. Their structures are all different from each other [13]. The detailed structural information of the collagens was gradually provided by different approaches, including electron microscopy, biosynthesis, immunology, and molecular biology methods [7]. Generally, all collagens have a triple-helical domain. The formation of the triple-helical structure is different from that of globular and nonhelical structures. The collagen molecules are synthesized intracellularly and then secreted



**Figure 2.1** Collagen triple-helix structure. Source: Reproduced with permission from Chmielewski [19]; © 2020, John Wiley and Sons.

into the extracellular space. After aggregation with other molecules, supramolecular structures are formed and stabilized by intermolecular covalent bonds [7].

## 2.2 Structure and Composition of Collagen

Collagens are the major components of connective tissues. They also exist in the interstitial tissue of parenchymal organs. The collagen ensures the stability and structural integrity of the tissues and organs. The role played by collagen in a specific organ determines its type and organization [14]. The collagen-enriched tissues include cartilage, tendons, cornea, and the organic component of bone. In tendons, collagen forms parallel fibers that support high strength. In the cornea, collagen is stacked to ensure the least scattering of transmitting light. In extracellular matrix, collagen exists in the form of a gel that maintains the tissue structure. In bone, collagen forms a framework with the hydroxyapatites, which show high mechanical performance as a composite material [15].

In terms of composition, collagen has a repeated motif of Gly–X–Y. Gly is glycine while X and Y are other amino acids. The positions of X and Y are mostly occupied by proline and 4-hydroxyproline, respectively [16, 17]. Although collagens with different types have different compositions, all of them have the same characteristics, such as a right-handed triple-helix structure containing three polypeptide chains [18]. As shown in Figure 2.1, the collagen molecule has a long and rigid structure composed of three  $\alpha$  chains that intertwine with each other to form a triple helix [19]. The collagen molecule shows a length of  $\sim 300$  nm and a diameter of 1.5 nm. The collagen fibers have high tensile strength because of the tight coupling  $\alpha$  chains, which is higher than that of a steel wire.

Based on the genetic type, the triple-helical motif can further form a major or minor part of the collagen molecule. In addition to collagenous domains, different noncollagenous parts also exist in the other regions of the collagen [20]. Specifically, three left-handed helices form a supercoiled right-handed structure in a rope-like shape [21]. It should be noted that the three chains are also staggered by one residue relative to one another [22]. On the whole, the collagens are composed of continuous triple helix and short-helical telopeptides. The telopeptides do not have triple-helical structures without repeating Gly–X–Y units. Although the telopeptides only account for 2% of the collagen molecule, they are essential to the formation of collagen fibrils [23].

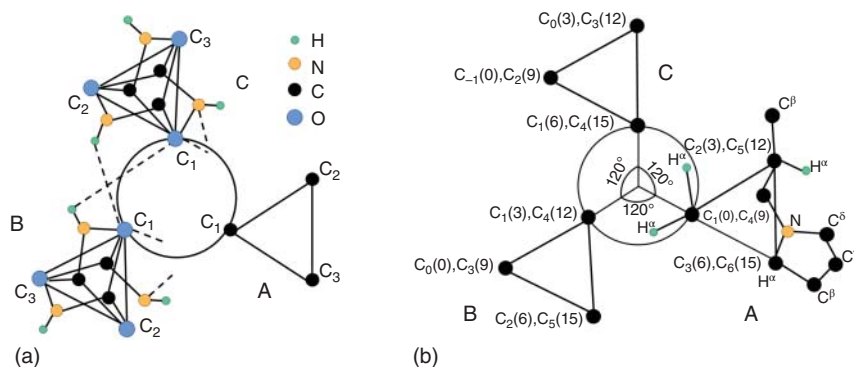
### 2.2.1 Amino-Acid Residue and Triple-Helix Structure

As mentioned above, the composition units of the collagen are amino-acid residues, which were found early in the 1940s. Early studies have already shown that the general nature of the amino-acid composition has a high uniformity although the collagen comes from different sources.

Each peptide of the collagen has ~1050 amino-acid units, including glycine, proline, hydroxyproline, and lysine residues [24]. Among these amino-acid residues, glycine and proline residues play important roles in the formation of the triple-helical structure. As the smallest amino-acid residue, glycine residue occupies every third position in the polypeptide chain. The specific position for the glycine is because that glycine residue is small enough to stably occupy the narrow core within the triple-helical structure. As a result, glycine residue accounted for about one-third of the total number of the chain residues, including mammalian, amphibian, and avian collagens [25]. In addition to glycine residue, proline and hydroxyproline residues are also important components of collagen, which account for ~25% of the amino-acid residues within the polypeptide chain. These two imino acid residues have a unique characteristic in that the C<sup>β</sup> atom is linked to the peptide nitrogen by the side chain, resulting in a 5-membered ring. The ring structures of proline and hydroxyproline residues act as “kinks” in the polypeptide chain, which are beneficial to the formation of the helical conformation. Specifically, the peptide unit links the amino-acid residue with the imino acid residue, leading to its low freedom degree of rotation about the N—C<sup>α</sup> bond. The restriction imposed on the orientation of the peptide unit can stabilize the collagen structure, endowing the collagen chain with high rigidity. As another amino-acid residue of collagen, alanine residue accounts for ~10% of all residues within the polypeptide chain. The other compositions (e.g. arginine, lysine, glutamic acid residues) in polar side chains account for ~20% of the amino-acid residues. Although these amino-acid residues are not very essential to the triple-helical structure, they play important roles in linkages of the triple chains to form the collagen fibrils [26].

It was known in early times that glycyI residues account for one-third of the total number of residues in the polypeptide chain. However, there was no specific structure to explain the content of glycine residue until 1954 [4]. Ramachandran and Reddi proposed the structure that glycine residue occupies every third position in the polypeptide chain. The position of glycine residue cannot be substituted by other residues that have β-carbon atoms. It is also assumed that all the peptide units in this structure should have their trans conformations, which is different from the previous structures. Figure 2.2a displays the projection of the triple-chain structure down the central axis [26]. The structure is composed of three polypeptide chains (marked as A, B, and C). Every polypeptide is in the shape of a threefold helix with a pitch of 9 Å. The helical chains are related to each other by a threefold screw axis, having a left-handed twist.

As shown in Figure 2.2a, the three chains are held together by hydrogen bonds [26]. In addition to the backbone of chain A, the atoms connected to the α-carbon atoms are also marked in Figure 2.2b [26]. It is shown that the bonds connecting



**Figure 2.2** Projection of the triple-helical structure of collagen. (a) Indication of the postulated hydrogen bonds between chains B and C. (b) Indication of the angles and heights of the  $\alpha$ -carbon atoms in the chains. Source: Modified from Ramachandran and Reddi [26]; © 1976, Springer Nature.

the  $\beta$ -carbon atoms to  $C_2^\alpha$  and  $C_3^\alpha$  point away from the triple-helix center, while the bonds connecting two hydrogen atoms to  $C_1^\alpha$  (as part of a glycine residue) point to the triple-helix center. It should be noted that there is no space for  $\beta$ -carbon atoms to form in this central region. If  $C^\beta$  occurred at position 1, the three chains would be separated from one another. In this case, the hydrogen bonds linking the chains could not be formed since the relevant bond length was too large to maintain stability. Therefore, it can be concluded that only the side chain of glycyl residue can be located at  $C_1^\alpha$  in the chains. Also, the residue at every symmetry-related atom (e.g.  $C_4^\alpha$ ,  $C_7^\alpha$ , etc.) can only be glycine. Thus, glycine residue must occur at every third position in the collagen chain to maintain the triple-helical structure. Different from position 1, it is easy to fix a prolyl side chain at position 2 or 3. The dihedral angle for proline residue has a limited range, which is perfectly satisfactory in the above structure. It should be noted that the positions 2 and 3 are not always occupied by imino acid residues (proline and hydroxyproline residues) although they can be fittingly located at these positions without distorting the main structure of the chains. Experimental evidence further confirmed the above speculation. A complete amino-acid sequence of one peptide chain showed that proline and hydroxyproline residues occur only in the positions 2 and 3. Moreover, it is revealed that hydroxyproline residue occurs only in position 3 while proline residue can occur in both positions. The unique occupation of hydroxyproline residue in the chain is very important to understand the hydrogen bonding within the triple-helical structure and the stability of collagen structure [26].

Engel and Bächinger further illustrate the triple-helical structure of collagen in detail. As shown in Figure 2.3, the three helices are staggered by one residue relative to each other, supercoiling along a common axis into a right-handed triple helix. The repeated sequence of Gly-X-Y is essential to the superhelical formation. There are three residues in the straight and non-supercoiled polyproline-II-helix every turn, while the residues of glycine are in the face of each other in the interior of the helix structure (Figure 2.3b) [27]. Since the side chain at the  $C^\alpha$  is larger than that at H,