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Introduction

Carbon cycle is the basic cycle on earth to maintain all the life forms. In the earth, there are four primary carbon pools [1]. Among them, the natural carbon cycle (NCC) mainly refers to the cyclic change of carbon in the three-carbon pools of atmospheric carbon pool, marine carbon pool, and terrestrial ecosystem carbon pool [1–4]. The atmospheric carbon has a direct influence on human life; therefore, it attracts great attention from researchers. The carbon in the atmospheric carbon pool mainly exists in the form of CO_2 gas. The basic process of the NCC can be expressed as follows [1, 5]: CO_2 in the atmosphere is solidified into organic carbon through photosynthesis of plants and stored in plants. Part of the organic carbon in plants releases CO_2 into the atmosphere through the plant's respiration (i.e. autotrophic respiration), the consumption of organic carbon by animals, and the decomposition of organic matter by microorganisms (i.e. heterotrophic respiration), forming a terrestrial ecology system carbon cycle process.

Since the industrial revolution and with the rapid world population/economic expansion, people utilized more and more fossil fuels for providing raw materials and electrical power, etc. [6]. Challenges in multiple environmental and ecological are emerging due to the overuse of fossil fuels and the increasingly severe energy crisis [7]. The results are that the NCC has been increasingly broken, leading to unavoidable sustainability in energy and environment, threatening the survival of human society. Thus, various strategies and various renewable energy technologies have been developed from all aspects to solve the broken NCC and maintain the sustainability of human society and the economy [8, 9]. These techniques include fuel cells, CO_2 electrolysis, metal-air batteries, water splitting, and so on. All of these techniques consist of the kernel and/or secondary components in artificial nature carbon cycle (ACC) to supplement for the NCC with synergistic effects [5, 7]. These techniques are mainly powered by solar-derived electricity, which were also defined as the artificial electrochemical carbon cycle (ECC). The ECC mainly involves electrochemical oxidation of chemicals and fuels into CO_2 (CO_2 liberation) and electrochemical reduction of CO_2 into value-added chemicals/fuels (CO_2 fixation), and also other fuel storage and transport, and other secondary reactions for supporting the carbon-based electrochemical reactions.

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For the realization of ECC, the extensive fundamental and utilitarian electrochemical processes, including oxygen reduction reaction (ORR), oxygen evolution reaction (OER), small organic molecule oxidation reaction, hydrogen evolution reaction (HER), hydrogen oxidation reaction (HOR), and electrochemistry carbon dioxide reduction reaction (ECDRR), were involved. In the water splitting processes [10], water oxidation (OER) occurs on the anode, and four-electron transfer is needed for a complete OER. At the same time, the generated electron and proton will be combined on the cathode and releasing H_2 from the cathode. In various fuel cells [11, 12], HOR via the two-electron transfer process and various small organic fuel (ethanol, formic acid, methanol, glucose oxidase, ethylene, glycerol, glycol, etc.) oxidation occur on the anode, while ORR takes place on the cathode. The cathode of metal-air batteries [13] also employs ORR processes. For the CO_2 electrolysis [14], CO_2 was electrochemically transformed into various fuels, as mentioned earlier, via different electron-transfer processes.

The generally sluggish reaction kinetics is always a bottleneck that limits the overall performance of the new energy devices, hindering their progress of commercialization [15, 16]. To drive these electrochemical processes, electrocatalysts are required. Noble metal catalysts are widely used in these electrocatalytic processes due to their high activity and stability. On the other hand, the high cost hinders their commercialization. Various non-noble metal catalysts were also developed, such as carbon materials, polymer, transition metal materials, and metal-organic materials [15]. With the development of nanotechnology and nanoscience over the past decades, the research mode for developing electrocatalysts has shifted gradually from the traditional trial-and-error methods to the accurate design and fabrication of nanocatalysts at atomic and molecular levels [15, 17, 18]. Besides, other factors in the electrochemical devices, such as the device structure, electrolyte, electrode configuration, and operation temperate, should be considered toward the high performance of the devices. Among these controllable factors, the electrocatalyst design is still among the core factor. To achieve the rational design of electrocatalyst for highly efficient electrocatalytic reaction processes, studies on the active sites' recognition, reaction mechanism, and kinetic and thermodynamic processes should be conducted. In this sense, computational methods combined with in situ characterization techniques allowed the researcher to realize an in-depth and comprehensive understanding of realistic reaction conditions into the nature of the active sites and its interaction with reactants, intermediates, and products and the final overall catalytic processes.

In this book, we will discuss the reaction mechanism and core reaction parameters (e.g. turnover frequency [TOF], onset potential or overpotential, stability, Faradaic efficiency, partial current density) of these electrochemical reactions strongly to the ECC and summarize the advances of various catalysts in terms of the categories to gain an overview on the design principles for electrocatalysts toward various electrochemical reactions. The device categories and advances will also be summarized, with respect to the electrolyte, device structure, electrode, and external environment controls. Then, theoretical calculations for these electrocatalytic reactions were introduced in terms of background, concepts, processes, and applications. Besides, an overview of the common and the most crucial in situ characterization techniques was summarized to assist the theoretical calculations study and help the electrocatalyst design. Further, we have summarized the advances on electrochemical reactions highly related to the ECC, that is, ECDRR, and fuel oxidation for the chemical conversions including CO_2/CO, CO_2/HCOOH, CO_2/CH_3OH, and CO_2/CH_3CH_2OH, along with presenting the mechanistic understanding and proposed key indexes, general principles, and external managements for evaluating and optimizing the overall ECC efficiency. Finally, current challenges and future perspectives for promoting ECC to supplement NCC were concluded. It is believed that this book will provide a comprehensive, deep-going, and cutting-edge introduction on the ECC and related electrocatalysis.

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