



Physicochemical properties and application process of nanomaterials in electrochemical energy storage system of Lithium-ion batteries (LIBs)

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Abstract

Growth of new energy industry puts forward new requirements for electrochemical energy storage technology. Since nanomaterials have many physical and chemical properties related to the composition and size, the application of nanomaterials in the area of energy storage with electrochemistry has unique advantages. The paper presented the application process of nanomaterials in super capacitors, Lithium-ion batteries(LIBs) and flow batteries, and analysed mechanisms of improving energy storage properties. The author found nanomaterials are mainly used for the structure and composition adjustment of electrode materials. Nanomaterials with special structures and large specific surface area can facilitate electrolyte penetration and electron transfer in supercapacitors. In lithium-ion batteries(LIBs), the specific capacitance and structural stability of positive electrode materials can be improved by doping and coating. Dispersing nanoscale catalysts on negative electrode materials can reduce electrochemical polarization and improve energy efficiency of flow batteries. The paper can offer theoretical direction for the applying nanomaterials in electrochemical energy storage systems, and guide the future development of new energy industry.

Keywords: Nanomaterials, electrochemicals, lithium-ion batteries, application, electrode materials, physical and chemical properties

Introduction

The 21st century, due to rapid development of social economy, steep growth of population and constant changes in the international situation, energy and environmental problems have become increasingly prominent. Mankind is simultaneously facing a shortage of almost all fossil fuels, including coal, oil, and natural gas, *et al.* Meanwhile, burning fossil fuels emits a lot of CO₂, which aggravates the greenhouse effect and cause a series of environmental problems, such as global warming and extreme weather. Therefore, the new energy industry is developing rapidly worldwide. However, the new energy, such as solar energy, wind energy and water energy, has characteristics of discontinuity, instability and uneven distribution. The electricity generated by it cannot be directly incorporated into the power grid, and has to be stored, converted and output by technologies for energy storage [1]. Among an assortment of energy storage technologies, the electrochemical energy storage technology has shown great potential by virtue of stability, low cost, high efficiency and wide applications. Nevertheless, the energy density, safety and cost of the electrochemical energy storage technology yet cannot meet the use requirement at present. Nanomaterials have many physical and chemical properties related to the composition and size, and are increasingly showing unique advantages in electrochemical energy storage. The manuscript deals with the application process of nanomaterials in supercapacitors, Lithium-ion batteries(LIBs) and flow batteries. Meanwhile, mechanisms of improving energy storage properties were analysed. Finally, the application prospect of nanomaterials in the area of electrochemical energy storage was prospected. Recently the role of surface modification in enhancing

electrochemical properties for battery applications [2] and investigation of transition metal oxide nanomaterials as electrode sodium ion batteries [3] has been described.

Materials and Methods

Supercapacitor: Supercapacitors consists of three parts: electrodes, electrolytes and separators. Depending on various energy storage processes, supercapacitors fall under the category of electrical double-layer capacitors (EDLCs), hybrid supercapacitors (HSCs), and pseudocapacitors.

EDLCs: The electrical double-layer capacitor stores charge through electrostatic adsorption at the electrode/electrolyte interface and forms a double-layer structure. Theoretical calculation and in situ characterization demonstrate that the energy storage properties of EDLCs are related to the surface area, pore size and microstructure of electrode materials.

Pseudocapacitor: The pseudo capacitor stores charge through the rapid and reversible redox reaction process at or near the surface of active substances. pseudo capacitors can be categorized as adsorption type, surface redox type, and intercalation type based on various energy storage processes. Adsorption pseudo capacitance is produced by the Faraday charge transfer process that occurs when atoms are adsorbed on the surface of conductive electrodes. Surface redox pseudocapacitance is produced by the rapid and reversible electron transfer process that occurs when cations are absorbed on the surface of oxides. The energy storage properties of surface redox pseudocapacitors are related to the surface area, crystal size and frame connectivity of electrode materials. Intercalation

pseudocapacitance is produced by the Faraday charge transfer process that occurs when metal cations are inserted into the pore or layer structure of active substances. The energy storage properties of intercalation pseudocapacitors are related to the pore structure and conductive characteristics of electrodes.

HSCs: The hybrid supercapacitor consists (HSCs) of a battery electrode and a capacitive electrode with different charge storage mechanisms. Therefore, HSCs have high energy and power density. The energy storage properties of HSCs are related to the morphology and conductivity of electrode materials. Through the analysis of the energy storage processes of different supercapacitors, the paper found increasing the specific surface area and conductivity of the electrode materials is essential to enhancing the energy storage capabilities of supercapacitors. In this paper, the application progress of carbon-based nanomaterials, transition metal oxide nanomaterials and nanocomposites in supercapacitors is reviewed according to different material types.

Carbon-based nanomaterial

Carbon nanotube: CNTs/CC electrode is prepared by in-situ growth of carbon nanotubes (CNTs) on carbon cloth (CC) by microwave plasma chemical vapour deposition (MPECVD) [4]. Nanostructure with a homogeneous dispersion of pore sizes and a large specific surface area, forming appropriate ion channels, which are beneficial to the transport of ions in electrodes. Therefore, supercapacitors composed of CNTs/CC electrodes possess a high density of energy and an extended cycle life. Moreover, CNTs/CC electrode can be bent and used to manufacture large, flexible, electrochemically stable supercapacitors.

Graphene: rGO/COF electrode material is prepared by introducing covalent organic framework (COF) into reduced graphene oxide (rGO) by hydrothermal method [5]. COFs can prevent the accumulation of graphene nanosheets, which ameliorate the stability of ion channels, thus improve the efficiency of ion transfer in electrolytes and electrodes. Therefore, supercapacitors composed of rGO/COF electrodes have high energy density.

Transition metal oxide nanomaterial: The preparation of RuO₂-CNTs-CC electrode material involves a single step of chemical vapor deposition (CVD) and annealing, wherein RuO₂ nanorods are used to modify carbon nanotubes grown on carbon cloth (CNTs-CC). With a large specific surface area, the multi-layer microporous or mesoporous network facilitates ion diffusion and electron transfer. In addition, transition metal oxides have large theoretical specific capacitances. Therefore, RuO₂-CNTs-CC electrode has a large specific capacitance [6].

Nanocomposite: ZnO-CoSe₂(ZOCS) nanosphere composite electrode material is prepared by selective reaction strategy. Because of its particular surface area and abundant active spots, nanosphere structure facilitates charge transfer and electrolyte penetration. Therefore, ZOCS nanosphere composite electrode can facilitate the redox reaction and improve electrochemical performance [7].

Results and Discussion

Lithium-ion battery: Lithium-ion batteries include electrodes, electrolytes, separators, current collectors, battery shells. The energy storage process of Lithium-ion batteries. Electrical and chemical energy are successfully converted by the electrochemical redox reaction of active chemicals in electrodes. Safety performance and energy density are the principal properties of lithium-ion batteries. The main direction of improving the safety performance is to replace traditional liquid electrolytes with solid electrolytes, which can fundamentally solve the problems of easy decomposition and flammability. The main direction of increasing the energy density is to improve the structural stability and specific capacitances of positive electrode materials, which can achieve a higher operating voltage and enable a higher proportion of lithium ions to participate in charge transfer. In this paper, the application progress of nanomaterials in positive electrode materials of lithium-ion batteries [8].

Composite nanoparticles of lithium phosphates and oxides: The surface of lithium cobalt oxide (LCO) particles can be evenly coated with lithium phosphate (LPO) and oxide composite nanoparticles by ultrasonic dispersion-mechanical agitation-high temperature annealing. The coating, in nanoscale can form interfacial protection on the surface of LCO particles. Thus, the interfacial charge transfer impedance is reduced and surface cracks and reconstruction are inhibited. Therefore, the electrochemical performance of LCO particles, especially the specific capacitance and structural stability, can be improved.

BiFe_{1-x}Mn_xO₃ nanoparticle: BiFe_{1-x}Mn_xO₃ nanoparticles are prepared by sol-gel method [9]. Mn doping in nanoscale efficiently introduces structural defects and oxygen vacancies, which can greatly hinder the growth of grains, reduce grain size and increase the degree of agglomeration. Thus, the volume expansion of electrodes is inhibited and the structural stability is improved. In addition, The amount of ions participating in the redox process can be efficiently controlled by the changing valence of Mn. Thus, the electrochemical reaction efficiency of electrodes is improved [9].

Flow battery: The flow battery consists of an ion exchange membrane, two electrodes, an electrolyte and two bipolar plates. The energy storage mechanism of the typical vanadium flow battery. The electrolyte formed by dissolving active substances in the solvent circulates between the storage tank and the battery by pump. During the circulation, active substances in the electrolyte can contact the electrode and undergo redox reactions to achieve the conversion of chemical energy and electric energy. The energy storage properties of flow batteries are related to ion selectivity, carrier pass rate, mechanical strength, electrochemical corrosion resistance of the ion exchange membrane, and the specific surface area, structural stability, electrical conductivity, electrochemical reactivity, electrochemical stability of electrode materials. A large specific surface area can provide more reactive sites, thus reducing the electrochemical polarization of the battery. A stable structure can ensure the fluidity of the electrolyte, thus reducing the concentration polarization of the battery.

In this paper, the application progress of nanomaterials in negative electrode materials of flow batteries is reviewed.

Bi-nanoparticle dispersed carbon felt: Bi-nanoparticle uniformly dispersed carbon felt is prepared by electrodeoxidation process with 1.6 V in alkaline solution. The addition of Bi nanoparticles, which is an electrocatalyst for V^{3+}/V^{2+} redox reaction of the negative electrode in vanadium flow battery, can significantly promotes energy efficiency and effectively inhibits the hydrogen evolution reaction. Meanwhile, the large specific surface area and abundant active locations of Bi nanoparticles can enormously reduce the polarization of vanadium flow batteries electrochemically.

Ti₃C₂T_x nanosphere: Ti₃C₂T_xPMMA nanospheres are prepared by stirring and centrifugation, and Ti₃C₂T_x hollow nanospheres are prepared by annealing in argon atmosphere to remove PMMA [10]. The thin wall of the hollow nanosphere is multi-layer Ti₃C₂T_x MXene, which can be used as the electrocatalyst of V^{3+}/V^{2+} redox reaction. MXene, a two-dimensional nanomaterial, on the other hand, possesses a large specific surface area, exceptional mechanical qualities, and good conductivity. Therefore, the graphite felt electrode modified by Ti₃C₂T_x nanospheres has an extended cycle life and exhibits excellent energy efficiency.

Conclusion

Nanomaterials have unique advantages and great application potential in the area of energy storage with electrochemistry, and have a significant impact on the optimization of energy structure, the enhancement of energy utilization efficiency and environmental protection. The paper summarized energy storage mechanisms and improvement strategies of energy storage technologies with electrochemistry, including flow batteries, lithium-ion batteries and supercapacitors. Meanwhile, the application of nanomaterials in electrochemical energy storage technology was discussed. In supercapacitors, electron transfer and electrolyte penetration can be facilitated by nanomaterials with unique structures and large specific surface area. In lithium-ion batteries, the specific capacitance and structural stability of positive electrode materials can be improved by doping and coating. In flow batteries, electrochemical polarization can be decreased and energy efficiency can be increased uniformly dispersing nanoscale catalysts on negative electrode materials. Nanomaterials are mainly used for the structure and composition adjustment of electrode materials nowadays, and are expected to have a wide application prospect in electrochemical components such as bipolar plates, current collectors and electrolytes in the future. Moreover, in order to achieve large-scale applications, the yield of nanomaterials needs to be further increased. The paper can offer theoretical direction for applying nanomaterials in electrochemical energy storage systems of Lithium ion batteries (LIBs) and guide the upcoming evolution of new energy industry.

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