



REVIEW

Research Progress in Nano-Structured MnO₂ as Electrode Materials for Supercapacitors

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Manganese dioxide has been considered to be promising electrode materials for supercapacitors in terms of its abundant storage, low cost and superior electrochemical performance. Synthetic methods of preparing nano-structured MnO₂ were summarized systematically and the recent developments were reviewed. The methods involved hydrothermal synthesis, sol-gel, chemical co-precipitation, low-temperature solid-state synthesis, electro-deposition, microemulsion, pyrolysis and microwave synthesis. Moreover, the solutions to improve the specific capacitance, electric conductivity and stabilization by doping or composite with carbon materials, metals and conductive polymers were also discussed. Finally, it indicates in the article that composite MnO₂ electrode materials will become the main trend in future researches.

Key Words: MnO₂, Supercapacitor, Electrode material, Doping, Composite.

INTRODUCTION

Supercapacitors are a new kind of energy-storage device developed in recent years. Its specific energy is almost 100 times larger than normal capacitors. It also has larger specific power and longer cycle life than batteries. The energy density of supercapacitors is only 1/10 of chemical power sources, but the power density is more than 10 times of that. Simultaneously, it is environmentally friendly, belonging to green energy. On the basis of the above advantages, supercapacitors have been widely used in electron, communication, national defense and aerospace, *etc.*¹ With the development of researches and techniques, supercapacitors will have a quite broad prospect of market.

Among numerous researches on supercapacitors, a considerable amount of work has been centred on electrode materials with high specific energy and specific power, which influence the performance of capacitors directly. At present, most attention has been focused on some precious metal oxides, such as RuO₂² and IrO₂³, which have high capacitance and good conductivity, while the high price is the main limiting factor. So searching for the materials with comparative performance but lower price becomes a research focus⁴. Nowadays, the problems of resources and environment have become increasingly evident.

Manganese dioxide has caused people's extensive concern and have a great potential for development as electrode materials, which possesses excellent performance, abundant reserves, low price and good environmental compatibility.

Manganese dioxide first used in supercapacitors was in 1999 by Lee and Goodenough⁵. Since then, domestic and abroad scholars have done a mass of researches around MnO₂ electrode materials and have made great process. Broughton and Brett⁶ use the method of sputtering deposition to produce manganese films and then form manganese oxide with porous dendritic structure by anodic oxidation. At a constant charging/discharging current density of 160 μA/cm² current, its specific capacitance can reach to 700 F/g, close to that of RuO₂. Although the current density is small, it is still a highly promising electrode materials as supercapacitors.

Manganese dioxide has many crystal forms such as α, β, γ, δ, λ *etc.* Different crystal form means different crystal cell structure, morphology and dimension, so there is difference in electrochemical performance. The properties of MnO₂ electrode materials have a close relationship with the preparation methods. Different preparing technique gets different crystal structure, micro-morphology and specific surface area, which intimately affect the charging/discharging capacitance. By summarizing and analyzing the related literatures, this paper

described the recent development of MnO₂ electrode materials prepared by different methods. There was a brief summary and review on the structure characteristics, performance and modified work, and then, the prospect of MnO₂ applied to supercapacitors was introduced.

Synthesis of nano-MnO₂ electrode materials: Crystals at nanoscale have higher specific surface area and more active sites than that at microscale, so it is extremely important to explore the optimal synthesis method. Methods of preparing nanometer MnO₂ include hydrothermal synthesis, sol-gel, electrochemical deposition, coprecipitation and micro-emulsion method, *etc.* The crystal structure and morphologies are related with the synthesis method. So far, there are many shapes of MnO₂ have been prepared, like rods, tubes, spheres, cubes and fibers and their properties are also different.

Hydrothermal synthesis: Hydrothermal synthesis is an effective method in inorganic synthesis and material processing. In a specially designed autoclave, aqueous solution is always used as the reaction medium. A relatively high temperature and pressure are created by heating and pressing the reaction system (or autogenic vapor pressure), which will help the insoluble or uneasily soluble material dissolve and recrystallize.

The hydrothermal method has many advantages in synthesizing functional nanomaterials: (1) the reaction temperature is obviously lowered, usually at 100 to 240 °C. (2) The synthesis and crystallization can be accomplished at one step. (3) The ratio of the products can be controlled. (4) It can be used to produce single phased material. (5) It is easy to produce integrated crystal with good-orientation. (6) Homogeneous doping can be easily performed in the crystal growing. (7) The environment of the crystal growth could be controlled. (8) The cost is relatively low.

Qi *et al.*⁷ produced MnO₂ with various crystal forms different materials by hydrothermal method. The urchin-like γ -MnO₂ was synthesized from MnSO₄ and (NH₄)₂S₂O₈ with equimolar and the nanowire-like α -MnO₂ was prepared from KMnO₄ and MnSO₄ with the mole ratio of 3:2. Both of that have good capacitance in 2 mol/L (NH₄)₂SO₄ electrolyte and the capacity was 244 and 159 F/g, respectively at the discharging current density of 2 mA/cm². It shows that MnO₂ with various crystal forms and morphologies could be produced by controlling the reactants under the same condition.

Deng *et al.*⁸ produced rod-like α -MnO₂ by hydrothermal method using KMnO₄ and Mn(CH₃COO)₂ as reactants and the diameter was about 50-70 nm. The product was uniformly shaped and well dispersed. They had good pseudo capacitance and power characteristics in the range of -0.5 to 0.4 V (*vs.* SCE). The capacitance was as high as 413 F/g at the current density of 10 mA/cm².

The particles produced by hydrothermal method have a series of advantages, such as integrated crystal, small size, uniform distribution and slight agglomeration. The appropriate stoichiometry and crystal forms are easily acquired. Therefore, the technique is admitted as a promising way to produce nano powders. However, hydrothermal method has some obvious limitations. The reaction time is relatively long and the system need to be proceeded at high temperature and pressure. A good seal of the autoclave is the prerequisite, which

makes the reaction invisible. So the adjustment of reaction parameters can only be achieved by detecting the product.

Sol-gel method: Organic or inorganic compounds of metals are used as precursors in the sol-gel method. The precursor dissolved in the solvent to form homogeneous solution. The solute acts with the solvent or other solute and the products agglomerate to particles of several nanometers then form stable sols. After evaporation, the sol transforms into the gel. Finally, oxide materials gained by sintering the gel at certain temperature. The pH, temperature, reaction time and the concentration of the solution are important factors during the reaction, which should be controlled in practical application.

At present, non-alcohol salt is usually used in the synthesis of nano MnO₂ and citric acid is used as the chelating agent. Metal ions will be mixed at atom level through the chelating of citric acid and metal ions. Meanwhile, the hydroxyl and carboxyl polymerize and gradually form solid gel, then nanometer MnO₂ will be obtained⁹.

Han *et al.*¹⁰ mixed citric acid with manganese acetate at the ratio of 1:0.4 and prepared nanometer MnO₂ by sol-gel method. Charging and discharging tests were performed in neutral, alkaline and acidic electrolyte, respectively. The results show that the MnO₂ electrode has the highest potential window (1 V) and specific capacitance (120.3 F/g) in 7 mol/L KOH solution, proving that KOH solution is more suitable as the electrolyte for super capacitors.

Anderson *et al.*¹¹ used KMnO₄ to oxidize Mn(ClO₄)₂ into MnO₂ sol at pH = 10.5 and prepared MnO₂ thin-film electrode by dipping and dropping method. In the electrolyte of 0.1 mol/L Na₂SO₄, the product produced by dipping reached a specific capacitance of 698 F/g and the reduction was less than 10 % after 1500 recycles. The disadvantage was that the time of galvanostatic discharge was too short (1-4 s). Nevertheless, the result shows that MnO₂ has a high potential capacitance, thus having attracted many scholars to explore it.

Sol-gel method requires simple equipments and can realize the chemical control at molecular level and geometry control at mesoscopic level. Thus the product has good chemical homogeneity, high purity and fine particles. It is easy to produce multi-component oxide film and the thickness of the film is easy to control. The disadvantage is that the gel process is slow and the synthesis period is long. Additionally, the agglomeration is always happened in the heating process.

Chemical coprecipitation: In the aqueous solution of metal salts, usually KMnO₄, with the control of appropriate conditions and the participation of metal cation reductant (MnSO₄, MnCl₂ and Mn(OAc)₂, *etc.*), nanoparticles will be obtained.

Nam and his colleagues¹² got nanowire structured MnO₂ by chemical coprecipitation, using KMnO₄ and MnCl₂. After cyclic voltammetry tests, they found that the specific capacitance in the gel electrolyte containing silica was higher than that in Na₂SO₄ electrolyte. After 1000 cycles, its specific capacitance still reached 151 F/g.

To prepare nano-structured MnO₂ by the method of chemical coprecipitation has the advantages of simple process and device, low synthesis temperature, high yield, low cost and easy to operate, *etc.* But the disadvantage is that it is easy

to form hard aggregates. However, the problem can be solved by controlling the concentration of reactant and the pH value of solution. Therefore, chemical coprecipitation is an important technology at large scale and low cost.

Low-temperature solid-phase synthesis: It is developing rapidly in recent years in the field of preparing nano-structured MnO₂ by the method of solid phase synthesis at low temperature or room temperature. Solid phase synthesis is to mix solid materials directly, then to get the product by chemical reaction through grinding. It starts with the diffusion and contact of reactant molecules then the reaction and generation products at last. At the moment, products disperse in the reactants, which are only the existence of impurities or defects. Only when the product molecules accumulate to a certain product size, crystal nuclei appear and the nucleation process finishes. When nuclei grow up to a certain size, single crystalline phase of the product appears. Thus solid-phase reaction contains 4 stages, which are diffusion, reaction, nucleation and growth. Because the reaction rate in different reaction system or the same reaction system but different conditions is different, it makes the characteristic of each stage illegible. So the total reaction characteristic is decided by the rate-determining step. For a long time, it is always thought that diffusion and nucleation are rate-determining steps in high-temperature solid phase reaction. The reason is that at high temperature, chemical reaction is rather fast, so it can't be the rate-determining step of the whole solid phase reaction. However, at low temperature, chemical reaction may be the rate-determining step.

It is reported by Zhang and Zhang¹³ that amorphous structured nano-MnO₂ was synthesized by solid phase reaction under 60 °C, through mixing potassium permanganate and acetic manganese at a certain proportion. The MnO₂ electrode had good Faraday capacitance and its specific capacitance reached 325 F/g in 1 mol/L KOH electrolyte.

Yuan and his colleagues¹⁴ selected different manganese source such as MnSO₄ and MnCl₂ to react with (NH₄)₂C₂O₄ at room temperature, respectively. From solid phase synthesis, the precursor of MnC₂O₄ was obtained. After calcined at 400 °C, MnO₂ was produced. After the test, the one prepared from MnSO₄ had higher specific capacitance of 362 F/g.

It has many advantages of low-temperature solid-phase synthesis, such as high yield, no solvent, good selectivity and little environmental pollution. Additionally, the shortages of conglomeration, long crystallization time and impurity caused by intermediate steps and high temperature are greatly reduced. It provides a low cost and simple method for the synthesis of nano-materials. Manganese dioxide is sensitive to experimental conditions, such as temperature and grind. So it is difficult to synthesize the MnO₂ crystal with high purity and low conglomeration.

Electrochemical deposition: Electrodeposition proceeded in the solution contained deposit ions. Ions will deposit evenly on the anodic or cathodic electrode plates by controlling the deposition rate and films with different density will be obtained. It can get electrode materials with the grain size of 1 to 100 nm at relatively simple conditions, which also has greater density, smaller porosity, excellent corrosion resistance and

high-temperature resistance. Therefore, electrodeposition is a promising method to prepare nano-materials.

Wang *et al.*¹⁵ prepared nano-MnO₂ by galvanostatic electrodeposition, constant-voltage electrodeposition or cyclic voltammetry electrodeposition, respectively. They also studied the influence of the three methods on the capacitance of MnO₂. Among them, the sample prepared by galvanostatic electrodeposition had the highest capacitance of 306.75 F/g in 0.3 mol/L Na₂SO₄ electrolyte. The author and her group used pulse electrodeposition to prepare MnO₂ electrode materials and the specific capacitance of the prepared sample could reach 311 F/g at the current density of 4 mA/cm₂.

The electrochemical deposition overcomes the shortcomings of the coating method and it is more convenient. The main disadvantage of this method is that the particle size is a little larger. Additionally, the thickness of films is not even enough and cracks will appear after heat treatment. It will be solved by controlling the deposition rate including current density and solution concentration. And dense or porous films could be got.

Micro-emulsion method: Micro-emulsion is transparent liquid composed of water, oil, surfactant and cosurfactant, which is a stable thermodynamic system. The preparation principle is that to form micro-emulsion with metal salts and precipitant agent. The nucleating and growth of colloidal particles are controlled in a smaller micro reaction zone. So the size of droplets is usually controlled at the nanoscale and the size of corresponding products is also limited at the nanoscale.

Sharma *et al.*¹⁶ synthesized MnO₂/C composite by the method of micro-emulsion. The specific capacitance of the electrode was 165 F/g in 0.5 mol/L Na₂SO₄ solution and MnO₂ was *ca.* 458 F/g.

This operation is simple and easy to achieve the continuous production. The products have controlled particle size, good dispersion and little size distribution, which are obvious advantages. It shows extremely broad application prospect among so many methods of nanoparticles' preparation. But the cost is higher due to the use of a large amount of surfactant in this method. Simultaneously, the agglomeration of particles often appears.

Pyrolysis: The pyrolytic method is to prepare MnO₂ by the thermal decomposition of manganous salts or manganese oxides with other crystal forms at a certain temperature. It is often achieved by the thermal decomposition of KMnO₄.

Liu and Zhang¹⁷ has obtained MnO₂ as electrode material for supercapacitors, by thermal decomposition of KMnO₄. The capacitive properties of thermal decomposition products at different temperatures were also studied. Among them, the performance at 550 °C is the best. In 0.5 mol/L Na₂SO₄ electrolyte, the specific capacitance can reach 243 F/g and keep steady, which remains more than 95 % of the capacitance after 200 cycles. It is due to its high ratio of amorphism/crystallization and Mn³⁺/Mn.

Microwave synthesis: In recent years, microwave technology is widespread in the synthesis of inorganic nanomaterials, because of its advantages such as simple process, low energy consumption, high yield, time saving and speediness, *etc.*

Microwave has strong penetrability and excellent selectivity. The way of heating system could make the reactants be equally heated, which can improve the structure and properties of the prepared materials. Besides, the time of microwave will directly affect the morphology and capacitance of nano-MnO₂¹⁸.

Doping and modification of MnO₂ electrode materials:

MnO₂ is a kind of semiconductor and has a high resistivity. The electron transfer impedance is higher during the redox reaction. However, single MnO₂ electrode material is still difficult to meet the requirements of practical applications, for the reasons like poor cyclic and rechargeable performance. Therefore, it is highly concerned currently of using synergies of different materials to obtain composite electrode materials with excellent performance. Now MnO₂ is doped with certain elements or substance through physical, chemical or electrochemical method, which will modify its properties, increase the utilization of active material and optimize the performance of charging and discharging. Presently, there have been a lot of researches in the field of screening additives, way of doping and the charging and discharging mechanism of modified electrodes. Many significant conclusions have been drawn.

MnO₂/C composite electrode materials: Carbon materials have many advantages such as large surface area, low internal resistance, good electrical properties and long cycle life. But single carbon materials or metal oxides still have some defects that are difficult to overcome. In order to give full play to the merits of carbon materials and MnO₂, researchers try to use carbon material as the carrier to prepare MnO₂/C composite electrode materials. Studies^{19,20} have shown that the contact between the carbon material and MnO₂ particles increases the amount of conductive channels in the electrode, which could increase the conductivity and reduce the equivalent series resistance of the system. So, the cycle performance of the electrode will be improved.

To adulterate carbon materials into MnO₂, there are two ways, physical doping and chemical doping. Lee *et al.*²¹ have studied their difference. For physical doping, although part of the carbon material coated on the surface of MnO₂, the combination between them is not close. For chemical doping, the synthesis of MnO₂ occurs on the surface of carbon materials and they bond together. The active region and specific capacitance of chemical doping is much larger than physical doping, about 3 times. Brousse *et al.*²² prepared MnO₂ through coprecipitation method and then mechanically mixed it with activated carbon. C/MnO₂ composite powders were obtained as electrodes for supercapacitors, whose capacitance was only 21 F/g. Because of the excellent performance of the chemical doping, numerous researches have been carried out. Doping materials are mainly activated carbon, carbon aerogels and carbon nanotubes, *etc.*

In a variety of porous carbon materials, activated carbon (AC) is abundant and inexpensive. However, as electrode materials, activated carbon is required not only larger surface area but also mesopore rate (2-50 nm)²³, so that materials will have good electrochemical performance. Wen *et al.*²⁴ prepared a thin layer of crystalline α -MnO₂/AC composite by *in situ* hydrothermal deposition, taking activated carbon as the carrier and MnSO₄ as the manganese source. α -MnO₂ had short-range

nanostructure with stable performance. It achieved efficient and reversible redox reaction through the tunnel effect (quantum effects), resulting in pseudo capacitance. It also produced synergy with the carbon carrier, thus had good electrochemical performance. The specific capacitance was 374.5 F/g at the current density of 3 mA/cm². It had good charging-discharging characteristic and cycle stability. After 1000 cycles, the capacitance retention could reach 95 %.

Carbon aerogel has porous network-like structure, high surface area and a wide aperture. Manganese dioxide active substance is easy to form composite on the surface or in the large aperture, so that active points of electrodes are increased and the specific capacitance will be improved. Besides, the conductivity of the composite is increased by carbon aerogel with high electrical conductivity. In addition, the performance of carbon aerogel is stable and the energy storage mechanism of electric double layer capacitors is not related to redox reaction, thus the cycle life of carbon aerogel is excellent. Therefore, the cycle life of composite material is better than that of MnO₂. Li *et al.*²⁵ got MnO₂/CRF composite material by chemical coprecipitation. The carbon aerogel base had pearl strings like, disordered and porous network structure with larger surface area and plentiful mesopores. MnO₂/CRF composite shows excellent capacitance, stable electrochemical performance and good reversibility in 6 mol/L KOH electrolyte. When the percentage of MnO₂ was 60 % in the composite, it reached the largest specific capacitance of 226.3 F/g. And the cycle performance was also good. The capacitance of MnO₂ electrode decreased 20 % after 400 cycles, while the composite electrode only decreased less than 9 %.

Carbon nanotubes (CNTs) have unique nano-sized hollow structure with large area and good conductivity. At present, more attention has been paid to compounding CNTs with other capacitor materials²⁶. Subramanian and his colleagues²⁷ prepared α -MnO₂/SWCNTs composite electrode by dispersing SWCNTs (the length less than 2 μ m and the diameter from 0.5-40 μ m) into KMnO₄ saturated solution and the stability of specific capacitance after long time cycling was studied. When the content of SWCNTs was 20 %, it could still keep 75 % of the capacitance after 750 cycles. But the capacitance of pure MnO₂ remained only 10 %, which proved that SWCNTs could reduce the internal resistance of particles, increase the reversible capacitance and improve the stability. Fan *et al.*²⁸ applied microwave to prepare MnO₂/MWCNTs composite material with the specific capacitance of 298 F/g at the current density of 2 mA/cm². In the research, MWCNTs played as the support of MnO₂, which restrained the transformation of nano-MnO₂ to rod-like structure.

Geim group²⁹ from Manchester University got thin layer graphene of two dimensions by mechanical exfoliation, enriching the carbon materials' family. Graphene is composed of single-atom layer of carbon atoms based on *sp*² hybridization. The basic structural unit of graphene is stable hexatomic ring and its theoretical thickness is only 0.35 nm, which is the thinnest two-dimensional material until now²⁹.

Because of higher specific surface area and special electronic conductivity³⁰, graphene has been widely applied in the field of supercapacitors and has drawn general attention

of researchers^{31,32} after successfully prepared. The composite of MnO₂ with graphene can effectively utilize the two-dimensional structure of graphene, enhance the conductivity and effective contact area of MnO₂, so the capacitive behaviour will be improved. Fan *et al.*³³, synthesized graphene-MnO₂ composite by depositing MnO₂ nanoparticles on the graphene surface through the microwave method. The compact interface contact between them enhanced the conductivity of the electrode and the contact area with electrolyte, which increased the utilization of MnO₂ greatly. The composite exhibited good reversibility and stability. At the charging/discharging rate of 2 mV/s, the specific capacitance could reach 310 F/g and the attenuation was only 4.6 % after 15000 cycles. The results indicate that graphene -MnO₂ composite has great potential in the field of supercapacitors. In addition, it also provides a fast, low cost and environmental method for the material's preparation.

At present, researches of carbon materials mainly focus on increasing the conductivity, reducing the equivalent series resistance and improving the specific capacitance and work voltage of the capacitor. During the development of carbon materials, there are mainly porous carbon, active carbon, active carbon fiber, carbon aerogel, carbon nanotubes and graphene, *etc.* And to increase the effective specific surface area and controllable pore size (> 2 nm)³⁴ will be the direction.

Metal doping: Mixed oxides formed from manganese and other metals can increase the power of alkaline metal ions and make the structure of active materials stable during intercalation/deintercalation of ions^{35,36}. This could not only improve the specific capacitance of manganese dioxide, but also decrease the attenuation during the cycle.

The metal additives have been reported are ions or oxides of Pb³⁷, Bi³⁸, Co³⁹, V⁴⁰, Ni⁴¹, Fe⁴² and Al⁴³ *etc.*

The crystal structure and discharge performance of MnO₂ are different from the kind of metal ions added. Each kind of ions has its unique function. For example, when ions or oxides of Bi or Pb are added, MnO₂ shows better reversibility during discharging, while, Co³⁺ or V⁵⁺ could prevent overcharge⁴⁴. The researchers have started widely researches on the influence of other metals' doping on the capacitance of MnO₂.

Feng *et al.*⁴⁵ prepared nano-MnO₂ doped with Cr by solid phase redox at low temperature. When the mole ratio of Mn and Cr was 100:1, it had the best discharge performance, whose capacitance was 70 % higher than pure MnO₂. It was due to the entry of Cr into the crystal of MnO₂, which made the lattice parameter of MnO₂ increase. It is beneficial to intercalation/deintercalation of H⁺. Moreover, Cr coated on MnO₂ and the extent of coating had a significant effect on the electrochemical performance of electrode materials.

Pang *et al.*⁴⁶ prepared Sn doped MnO₂ as electrode material for supercapacitors by liquid chemical method, of which crystal form was *d* type. Part of Sn coated on the surface of MnO₂ in the form of oxides and part of it existed among layers of δ -MnO₂. The results demonstrate that doping ratio play a key role in improving the capacitance. Only an appropriate ratio of Mn and Sn can produce synergy. When interlayer spacing of δ -MnO₂ increases appropriately, it is easy for intercalation/deintercalation of ions, which will improve the

specific capacitance effectively. When the mole ratio of Mn and Sn was 50:1, the specific capacitance reached 293 F/g at the current density of 0.2 A/g, which was 64.6 % higher than the undoped. After 600 cycles, the capacitance stabilized at 275 F/g, exhibiting good retention of capacitance.

Additionally, doped with rare-earth elements may be a better way. Chen and his colleagues⁴⁷ studied the performance of manganese dioxide doped with lanthanum oxide. The results show that the specific capacitance of composite is 54.6 % higher than pure MnO₂ and the efficiency is 19.5 % higher. Li *et al.*⁴⁸ synthesized MnO₂ doped with CeO₂ by chemical precipitation. When the mass ratio of CeO₂ and MnO₂ was 10 %, the capacitor had the best performance, which was 257.68 F/g at the current density of 250 mA/g. After 500 cycles, the capacitance of doping capacitor reduced 1.18 %, but that of the undoping reduced 4.4 %. The radius of La³⁺ (0.122 nm) and Ce⁴⁺ (0.094 nm) are both larger than that of Mn⁴⁺ (0.054 nm). The adding of rare-earth ions could support the lattice and increase lattice parameters, which is good for the diffusion of electrolyte ions. Simultaneously, it is able to stabilize the crystal structure of MnO₂ and decrease the production of Mn₃O₄ during discharging. Therefore, it has favorable stability and capacitance after metal doping⁴⁸.

Compounding with conductive polymers: Conductive polymers have good conductivity and pseudo-capacitance as new developing electrode materials for supercapacitors. They can work in the high voltage (3.0-3.2 V). It can remedy the defect that the work voltage of transition metal oxides is not high. Composite electrodes will be obtained by coating the conductive polymer on the surface of the prepared manganese oxide powder. Polymerization reaction occurs at the surface of manganese oxide powder to form the network-like structure, which can enhance the conductivity and pseudo capacitance of the electrode⁴⁹.

Rios *et al.*⁵⁰ deposited a layer of 3-methyl polythiophene conductive polymer (PMeT) on Ti substrate first, then a layer of MnO₂ by electrochemical deposition. By the method, PMeT/MnO₂ composite electrode were prepared. The specific capacitance of PMeT/MnO₂ composite was 218 F/g (based on the mass of MnO₂ was 381 F/g), in 1 mol/L Na₂SO₄ electrolyte, at the scan rate of 20 mV/s. It was much higher than pure MnO₂ (122 F/g). The increase of the capacitance was due to that the deposition of PMeT on the electrode changed its surface morphology. After the deposition of MnO₂, porous and rough surface was formed, which was beneficial to increase specific surface area of the electrode. So that, the specific capacitance increased.

Polyaniline (PANI) is a type of common conductive polymers, having reversible electrochemical activity, large specific surface area and good stability. Compared other conductive polymers, the synthesis of polyaniline is easy and the price is low cost, which has become the focus of researches on electrode materials for supercapacitors. Prasad and Miura⁵¹ obtained MnO₂/PANI composite electrode by depositing nano-MnO₂ on polyaniline substrate. By optimizing the thickness of polyaniline film and the mass of MnO₂, the specific capacitance of the composite electrode could reach 715 F/g. And the energy density was 200 W h/kg at the current density of 5

mA/cm². However, as a kind of special conductive polymer, conductive mechanism, doping mechanism and molecular structure of polyaniline is more complex. With the deepening of the research, the performance of polyaniline requires a higher level.

Conclusion

Researches on supercapacitors with high specific energy and specific power are still on the early period of industrialization. There is still a lot of work to do in the future. It is still key problems in the development of supercapacitors to develop electrode materials and preparation techniques of MnO₂ with good electrochemical performance for supercapacitors.

It is hot spots of current researches on manganese dioxide electrodes to find out the relationship between the performance of MnO₂ and its characters, such as structure, morphology and specific surface area, to further optimize preparation conditions, to explore more controllable methods, to enhance the specific surface area and hole capacitance of MnO₂ materials, to make a good contact with electrolyte and to improve the utilization of materials.

It will be the focus of future research to modify MnO₂ by doping or composite method, which will make up the deficiency of manganese dioxide and achieve the synergy. By this way, composite electrode materials with excellent performance will be obtained. International and domestic scholars have already carried a lot of work and made some achievements. It is expected that in the near future, manganese dioxide will get more extensive application in the field of supercapacitors.

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REFERENCES

- C. Liu, F. Li, L.P. Ma and H.M. Cheng, *Adv. Mater.*, **22**, E28 (2010).
- J.P. Zheng, P.J. Cygan and T.R. Jow, *J. Electrochem. Soc.*, **142**, 2699 (1995).
- A.A.F. Grupioni, E. Arashiro and T.A.F. Lassali, *Electrochim. Acta*, **48**, 407 (2002).
- C.C. Hu and T.W. Tsou, *Electrochem. Commun.*, **4**, 105 (2002).
- H.Y. Lee and J.B. Goodenough, *J. Solid State Chem.*, **144**, 220 (1999).
- J.N. Broughton and M.J. Brett, *Electrochim. Acta*, **49**, 4439 (2004).
- S.Y. Qi, J. Feng, J. Yan, X.Y. Hou and M.L. Zhang, *Chin. J. Nonferrous Met.*, **18**, 113 (2008).
- M.G. Deng, Y.H. Feng, Q. Fang and Y.F. Chen, *J. Functional Mater. Devices*, **15**, 503 (2009).
- C.A. Ma, Y.W. Lou, F.M. Zhao, Y.Q. Chu and Y.H. Zhu, *Chin. J. Nonferrous Met.*, **14**, 1736 (2004).
- E.S. Han, X.P. Zhang, H. Xu and Z.H. Feng, *Chin. Battery Ind.*, **13**, 219 (2008).
- S.C. Pang, M.A. Anderson and T.W. Chapman, *J. Electrochem. Soc.*, **147**, 444 (2000).
- H.S. Nam, J.S. Kwon, K.M. Kim, J.M. Ko and J.D. Kim, *Electrochim. Acta*, **55**, 7443 (2010).
- B.H. Zhang and N. Zhang, *Acta Phys.-Chim. Sin.*, **19**, 286 (2003).
- A.B. Yuan, X.L. Wang, Y.Q. Wang and J. Hu, *Energy Convers. Manage.*, **51**, 2588 (2010).
- X.Y. Wang, X.Y. Wang, C.Y. Hu, X.P. Li and T. Yi, *Nat. Sci. J. Xiangtan Univ.*, **31**, 47 (2009).
- R.K. Sharma, H.S. Oh, Y.G. Shul and H. Kim, *J. Power Sources*, **173**, 1024 (2007).
- X.M. Liu and X.G. Zhang, *J. Inorg. Mater.*, **18**, 1022 (2003).
- S.K. Meher and G.R. Rao, *J. Power Sources*, **215**, 317 (2012).
- X.P. Dong, *J. Phys. Chem. B*, **110**, 6015 (2006).
- S.B. Ma, Y.H. Lee, K.Y. Ahn, C.M. Kim, K.H. Oh and K.B. Kim, *J. Electrochem. Soc.*, **153**, C27 (2006).
- H.Y. Lee, S.W. Kim and H.Y. Lee, *Electrochem. Solid-State Lett.*, **4**, A19 (2001).
- T. Brousse, P.L. Taberna, O. Crosnier, R. Dugas, P. Guillemet, Y. Scudeller, Y.K. Zhou, F. Favier, D. Bélanger and P. Simon, *J. Power Sources*, **173**, 633 (2007).
- E. Frackowiak and F. Beguin, *Carbon*, **39**, 937 (2001).
- Z.B. Wen, Y.F. Liu, Z.H. Hu, Y.P. Wu, A.F. Liu, C.C. Wang and X. Xu, *Acta Chim. Sin.*, **68**, 1473 (2010).
- J. Li, X.Y. Wang, Q.H. Huang and C.L. Dai, *J. Functional Mater.*, **37**, 1938 (2006).
- J. Hu, A.B. Yuan, Y.Q. Wang and X.L. Wang, *Acta Phys.-Chim. Sin.*, **25**, 987 (2009).
- V. Subramanian, H.W. Zhu and B.Q. Wei, *Electrochem. Commun.*, **8**, 827 (2006).
- Z.J. Fan, Z.W. Qie, T. Wei, J. Yan and S.S. Wang, *Mater. Lett.*, **62**, 3345 (2008).
- K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva and A.A. Firsov, *Science*, **306**, 666 (2004).
- X.L. Zuo, S.J. He, D. Li, C. Peng, Q. Huang, S.P. Song and C.H. Fan, *Langmuir*, **26**, 1936 (2010).
- M.D. Stoller, S. Park, Y.W. Zhu, J. An and R.S. Ruoff, *Nano Lett.*, **8**, 3498 (2008).
- Y.W. Zhu, S. Murali, M.D. Stoller, A. Velamakanni, R.D. Piner and R.S. Ruoff, *Carbon*, **48**, 2118 (2010).
- J. Yan, Z.J. Fan, T. Wei, W.Z. Qian, M.L. Zhang and F. Wei, *Carbon*, **48**, 3825 (2010).
- R. Kotz and M. Carlen, *Electrochim. Acta*, **45**, 2483 (2000).
- J.J. Xu, J.S. Yang and G. Jain, *Electrochem. Solid-State Lett.*, **5**, A223 (2002).
- K.R. Prasad and N. Miura, *Electrochem. Commun.*, **6**, 1004 (2004).
- H. Kim and N.P. Branko, *J. Electrochem. Soc.*, **150**, D56 (2003).
- S.J. Li, S.L. Wang, B. Xu and H.F. Gao, *J. Chem. Ind. Eng.*, **59**, 514 (2008).
- X.M. Liu, X.G. Zhang, S.J. Bao and Y.G. Wang, *J. Functional Mater.*, **9**, 267 (2003).
- F. Zhang, K. Ngala and M.S. Whittingham, *Electrochem. Commun.*, **2**, 445 (2000).
- Y.S. Chen and C.C. Hu, *Electrochem. Solid-State Lett.*, **6**, A210 (2003).
- Z.Y. Tang, X. Geng, Z.L. Wang and J.J. Xue, *Chin. J. Appl. Chem.*, **19**, 936 (2002).
- E.S. Han, X.P. Zhang and H. Xu, *Inorg. Chem. Ind.*, **40**, 34 (2008).
- E. Kahraman, I. Binder and K. Kordesch, *J. Power Sources*, **36**, 45 (1991).
- Y.L. Feng, M.L. Zhang, Y. Chen, X.Y. Jing and Y. Han, *Chin. J. Nonferrous Met.*, **15**, 316 (2005).
- X. Pang, Z.Q. Ma and L. Zuo, *Acta Phys.-Chim. Sin.*, **25**, 2433 (2009).
- Y. Chen, M.L. Zhang, Y. Han, C.Q. Luo and Z.H. Shi, *Chin. J. Rare Met.*, **29**, 30 (2005).
- B.H. Li, S.H. Ding, K. Liang, K. Zhuang and J. Hu, *Electronic Components Mater.*, **25**, 4 (2006).
- Z.A. Zhang, B.C. Yang, M.G. Deng and Y.D. Hu, *J. Inorg. Mater.*, **20**, 529 (2005).
- E.C. Rios, A.V. Rosario, R.M.Q. Mello and L. Micaroni, *J. Power Sources*, **163**, 1137 (2007).
- K.R. Prasad and N. Miura, *Electrochem. Solid-State Lett.*, **7**, A425 (2004).