Research of MnCO_3/CB Composite on Properties Apply to Supercapacitors

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Abstract. In order to improve the electro-conductibility of new energy storage material-manganese carbonate(MnCO_3) and the properties apply to supercapacitors, we produce MnCO_3/CB composite at room temperature by using a simple and mild liquid phase deposition method. Using dilute HNO_3 to purify and activate the CB(carbon black), then put the handled CB into $\text{NH}_4\text{HCO}_3/\text{MnSO}_4$ mixed solution for liquid deposition. Observed through infrared and XPS methods, we found that - after purified by dilute HNO_3 , the negatively charged groups(carboxyl & quinonyl) on CB surface increase, which makes CB uneasy to reunite in water and benefits the producing of a homogeneous compound. Observed the compound under SEM:40nm diameter CB granules wrap the Lotus-shaped MnCO_3 granule, and form a porous structure between MnCO_3 granules. The result of electro-chemical properties indicated by galvanostatic charge-discharge tests shows that the specific capacity of MnCO_3/CB composite electrode material is twice of the pure MnCO_3 electrode material, while the MnCO_3/CB composite has a good cycle capacitive retention ratio. As a newly discovered energy storage material, MnCO_3 provides a new direction to make composite material for supercapacitor electrodes.

1 introduction

The supercapacitor is a new energy storage component intervenient by traditional capacitor and battery. With high power density, short charging time, long lifespan, good temperature property, energy saving and environmental protection features, it is a research priority and widely used in mobile communication, information technology, consumer electronics, electric automobile, aerospace technology, national defense field, etc.[1].

As an electrode material of supercapacitor, metal oxide produces pseudocapacitance via self-redox reaction with a higher specific capacity than double electric layer porous carbon material. In past researches, because of the high theoretic specific capacity, transition metal oxides draw the attention of vast researchers: the specific capacity of RuO_2 can reaches 720F/g, but it's polluting and too expensive to be widely used[2]. Comparatively speaking, manganese materials are well-accepted in electro-chemical field because it is easy to obtain and environment-friendly, such as $\text{Mn}(\text{OH})_2$ [3] and MnMoO_4 [4]. MnO_2 is the most popular material with an extraordinary specific capacity of 1370F/g[5]. Recently, Davaraj et al. [6] found that MnCO_3 also has energy storage property, the specific capacity reaches 216 F/g within 1 mol/L $\text{Mg}(\text{ClO}_4)$ electrolyte solution. However, the poor performance on electro-conductibility and charging-discharging reversibility limits the application prospect.

Many scientists try producing compounds to solve this problem[7]: they use conductive materials with a bigger specific surface area as a base and put active material onto it to form a three-dimensional structure. Conductive material can be an internal transmission channel to transmit electrons, which greatly increases the use ratio of active material and be a main solution. Graphene and carbon nanotube are generally used as conductive bases[8], however, massive stacking of C6 makes the original carbon structure possesses no defects, and then weakens the reactivity. Meanwhile, these two materials are too complex to produce for mass production. On the contrary, the CB selected in this research is covered by thin graphene layer, which spreads the defects of carbon material all over the surface and greatly increases the reactivity. Moreover, the high level of CB material's specific surface area, the 3D channel structure formed by stacking and the simple operation are also the reasons we choose CB for research.

For the first time, this research uses well-conductive small-sized CB granules(about 40nm in diameter) to wrap and connect the manganese carbonate granules (about 700nm diameter), and the CB granules form a porous 3D structure around the manganese carbonate granules. On electro-chemical properties, this composite doubles the specific capacity compared with pure manganese carbonate material and reaches 218F/g under 5 mV/s scan rate and the capacity retention ratio reaches 92% after 1100 times cycles, which overcomes dissolution shortcoming of metal oxides active material. This composite indicates a new direction for the

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application of manganese carbonate materials and broaden the application fields for carbonate materials.

2 Experiment Part

2.1 Main Reagents and Apparatuses

The mains reagents used in experiment include: NH_4HCO_3 (AR), MnSO_4 (AR), HNO_3 (AR).

The mains apparatuses used include: Philip XL30 field emission scanning electron microscope (FESEM) at 20kV acceleration voltage; Rigaku Corporation D/max X-Ray Diffractometer (XRD), $\lambda=0.15406\text{nm}$; Shimadzu TA-50 Thermal Gravimetric Analyzer (TGA), annealing in nitrogen atmosphere - $10^\circ\text{C}/\text{min}$.

2.2 MnCO_3/CB Composite Preparation

Handling commercial use CB (Vxc-72, $256\text{ m}^2/\text{g}$, Carbot) with dilute carbonic acid and sulfuric acid by hydro-thermal treatment for 3h at 80°C , then rinse CB with distilled water to a neutral pH. Weigh 0.15g purified CB, add a certain amount of water, after 30min ultrasonic processing to disperse it homogeneously, and weigh 2mmol MnSO_4 , add slowly to the aforementioned mixture and keep stirring for 3h until the reaction is over. Centrifuge the precipitate, rinse with distilled water to neutral, dry in vacuum and obtain the composite. add slowly to the aforementioned mixture and keep stirring for 3h until the reaction is over. Centrifuge the precipitate, rinse with distilled.

2.3 Electrode Fabrication

Weigh MnCO_3/CB composite and poly tetra fluoroethylene (PTFE) by fraction 95:5, put into absolute ethyl alcohol, disperse homogeneously via ultrasonic processing, dry in vacuum oven for 12h; press the material into 500 meshes stainless steel meshwork, then connect to nickel foam current collector to obtain the electrode slice. In electro-chemical tests, we use three electrodes testing method with 1 mol/L Na_2SO_4 electrolyte solution, take $\text{Hg}/\text{Hg}_2\text{SO}_4$ saturated electrode as reference electrode and Pt electrode as counter electrode.

3 Experiment Results and Discussion

3.1 The influence of dilute acid purification on CB surface's functional groups

In this experiment, commercial treat CB hydro-thermal with dilute carbonic acid and sulfuric acid at 80°C for 3h, aim to remove the metal and other impurities. After this progress, negatively charged groups (carboxyl and quinonyl) on CB surface is found to increase, as shown in Fig.1., which makes CB dispersed homogeneously in solution and benefits the producing of a homogeneous compound. In this research, infrared spectroscopy is

used to observe the change of negatively charged groups. From Fig.1., we know that the strong absorption peaks between $3000\sim 3400\text{cm}^{-1}$ are stretching vibration peaks of carboxyl and absorption peaks caused by KBr absorbing water. The weak absorption peak at 1047cm^{-1} indicates that the C-O single bond exists on CB surface and the strong absorption peaks between $1600\sim 1700\text{ cm}^{-1}$ belong to stretching vibration peaks of C-O double bond in quinonoid structure and -COOH structure. From infrared spectroscopy analysis, we make sure that CB after dilute acid handled has an increase of carbonyl, carboxyl and quinonyl groups, along with an increase of electronegativity, which benefits CB granules dispersed homogeneously in solution to produce a homogeneous compound.

Fig. 1. FT-IR spectrum of purified CB.

Infrared spectroscopy analysis in Fig.1. is qualitative analysis of functional groups on CB surface to understand the situation, then we use XPS electron spectroscopy to quantitatively analyze the negatively charged groups on purified CB surface. Peak-differentiating curve of C1s and O1s is in Fig.2. a) and b). The specific relevant peak area is shown in Table 1.

Table 1. Deconvolutional peak area percentages of C1s and O1s

Photoelectron	Peak Location/eV	Peak area percentage/%
C1s	290.3	9.6
	288.4	2.4
	286.4	29.7
	284.6	58.3
O1s	535.4	16.9
	533.2	71.9
	531.3	11.2

For C1s, there are four kinds of carbon atoms with different binding energy: atoms with binding energy 290.3eV belong to stronger electron-withdrawing group -COOH (adjacent to quinonyl group), taking 9.6% of whole carbon atoms. Atoms with binding energy 288.4eV belong to lactones or weak acid -COOH, taking 2.4%; atoms with binding energy 286.4eV belong to quinonyl, taking 29.7%, indicating a mass of quinonyl groups and a small number of carboxyl groups on CB surface and within the layers. The atoms with binding energy 284.6eV belong to fused ring structure of CB itself, taking 58.3%. For O1s, there are three kinds of oxygen atoms with different binding energy: the atoms

with binding energy 35.4eV belong to O_2 & H_2O absorbed on CB surface, taking 16.9% of whole oxygen atoms. The atoms with binding energy 533.2eV belong to C-O double bond, taking 71.9%[8]. The atoms with binding energy 531.3eV belong to C-O single bond. Through XPS and FT-IR characterizations, we conclude that the purified CB surface contains massive negatively charged groups(carboxyl and quinonyl etc.), which benefits CB granules dispersed homogeneously in solution to produce a homogeneous compound.

Fig.2. Deconvolutional peak spectrums of purified CB of a) C1s and b) O1s

3.2 Structural representation and morphology characterization of the composite

In order to determine $MnCO_3$ capacity within CB, thermogravimetric analysis was made on the composite. Fig.3. is the TGA curve in atmosphere of nitrogen, between 0~800 °C, under a heating rate of 10 °C/min. From the curve we know, at 350°C, the weight loss factor reaches 2.5%, corresponding to the physically absorbed water and interlayer water of sample have a loss factor of 21.5% between 350~800°C. Besides bound water loss, there is no other loss, according to literatures, we consider the loss is CO_2 escaped, so we can figure out the capacity ratio of $MnCO_3$ in compound is 60%[9] based on mass conservation equation.

Fig.3. TGA curve of $MnCO_3$ /CB composite under N_2 .

Fig.4. is the XRD diffraction pattern of $MnCO_3$ /CB and CB, we can know that the $MnCO_3$ crystal form in $MnCO_3$ /CB is Hexagon(JCPDS no.44-1472) from the angles indexed in correspondence with diffraction peaks. The peaks of composite are steep and sharp, proved good crystallinity of the composite $MnCO_3$. From the CB diffraction peaks, based on 2θ and half-peak width, we can calculate lattice parameter La of CB is 4.07nm, which parameter expresses the crystal size of CB. According to peaks of the composite, lattice parameter La of $MnCO_3$ can be calculated: $a=b=0.4790nm$, $c=0.17694nm$. Compared with standard size hexagon $MnCO_3$ (cell parameters is $a=b=0.4810nm$, $c=0.1575nm$), this lattice has an extension on Z-axis. This is because the flaw activity of CB surface and orientational change of layered structure, which make the size of crystal particles changed[10]. Compared these two patterns, we can see the peaks of CB is very inconspicuous, this is a result that the diffraction peak of CB at 25° and (021) peak of $MnCO_3$ have superposition, which causes preferential inductive effect showing a steep and sharp peak (021).

Fig.4. XRD results of $MnCO_3$ /CB composite and CB

Fig.5 is field emission scanning electron microscope (FESEM) pattern of $MnCO_3$ /CB composite, and EDS test result of corresponding part in Table.2, which aim to component analysis of the composite. From the results we know the big granules is $MnCO_3$ with a high content of C atoms and lower content of S atoms due to the existing of CB granules. As EDS result is the atoms content based on local surface instead of whole

composited, it can be used for qualitative investigation. From Fig.5, we can see the MnCO_3 crystal is spherical lotus-shaped with a diameter of 700~800nm, being wrapped and dispersed homogeneously in the flocculent conductive CB granules. Compared with sphere with smooth surface, contact area with electrolyte solution of lotus-shaped crystal is much bigger, which increases active sites for pseudocapacitance reaction and improve specific capacity. Fig.5 shows CB(about 40nm in diameter) granules stacking around MnCO_3 : they not only wrap MnCO_3 , but also connect each other to form a 3D porous structure; this structure benefits the transmission and conduction of electrons, also enables ions efficiently contact the material interior to improve the specific capacity of composite[11].

Fig.5. FESEM result of MnCO_3/CB composite and EDS result of corresponding part

Table 2. Result of EDS spectrum

Atom	C	O	S	Mn
Percentage /%	30.44	52.50	0.34	16.72

3.3 Synthesis mechanism analysis

Fig.6. The schematic illustration of preparation of MnCO_3/CB composite

Fig.6 is the schematic illustration of preparation of MnCO_3/CB composite. At first, the structure of CB granules is irregular polyhedral subsphaeroidal with strong reunion trend to form “botryoid” conjugate. The granules are 20~50 nm in diameter with stratiform graphene layer on it’s surface. Add dilute carbonic acid and sulfuric acid, after 3h hydro-thermal treatment at 80°C, aim to remove the metal and other impurities and increase negatively charged groups(carboxyl and quinonyl), which makes CB dispersed homogeneously in solution and benefits the producing of a homogeneous compound. After adding MnSO_4 & NH_4HCO_3 solution, negatively charged groups begin to immobilize the positive ions Mn^{2+} , as time goes on, precipitations are formed by CO_3^{2-} & Mn^{2+} and immobilized onto crystal by C atoms exposed on CB surface. Crystal grows for a period; although C atoms on CB surface participate in combination, other C atoms with defect keep immobilizing ions and make crystal grow bigger. This is the reason why MnSO_4 granule in composite is much bigger than MnSO_4 obtained merely from solution[12].

3.4 Electrochemical Characterization

To have a further conclusion on capacity property of MnCO_3/CB , we compare EIS between pure MnCO_3 and the composite, as shown in Fig.7a). EIS inspects material properties mainly from electrode kinetics aspect: data corresponding to left terminal located on semicircle of high-frequency area represents contact resistance of whole system. Radius of the semicircle represents transfer resistance(R_{ct}) of electrode charge-and-discharge. The straight line in middle-frequency area is Warburg impedance area, which represent diffusion resistance of electrolyte ion within electrode porous structure[12], as shown in Fig.7b).

Fig.7.a) Nyquist plots for MnCO_3 and composite, **b)** EIS equivalent circuit diagram.

Compared the two curves in Fig.7.a), we see that after combination with MnCO_3 and CB, impedance R_{ct} reduces from 1.23Ω to 0.53Ω in high-frequency area. This is because CB enables electrons transfer faster then remarkably improves the dynamical properties. The straight line in middle-frequency area also changes, length of Warburg impedance area decreases. This is because, after combination, CB granules stacking around MnCO_3 lower internal diffusion resistance of the active material.

As shown in EIS curve, internal resistance of composite decreases for better electrochemical properties. For a further study, we use cyclic voltammetry to test the capacity under different scan rate and investigate long-time cyclic stability after 1100 times cycling. As shown in Fig.8.

Under low scan rate, CV curve keeps rectangular, although polarization phenomenon occurs at both ends, the whole graph displays mirror symmetry which indicates wonderful reversibility. No obvious redox peaks appear on the curve, which indicates faradaic reaction of active material proceed stably. When electric potential changes, response current has faster action. This is because CB has good conductive property and 3D porous structure enables electrons move faster, which makes the electrons transmitted efficiently in time for a high reaction efficiency. Under 5 mV/s scan rate, calculate via cyclic voltammetry equation, capacity of composite is 218 F/g and capacity of CB is 57 F/g , which proves that the composite not only have the double-layer storage property of carbon material, but also have pseudocapacitance storage property of MnCO_3 . Compared with previous literature, the specific capacity of pure MnCO_3 material in $1 \text{ mol/L Na}_2\text{SO}_4$ electrolyte solution is 118 F/g [6], this capacity is almost twice of it. In order to investigate the stability, we test it's cycling performance.

Fig.8. CV curves of MnCO_3 /CB composite at different scan rates

In Fig.9, capacity decreases when scan rate increases. when scan rate raise to 300 mV/s , the capacity decrease to 46%. Capacity attenuation is mainly related with the decrease of active sites on electrode surface during fast charging-discharging. Compared with other metal oxids electrode, this composite has lower attenuation, because MnCO_3 solution is inhibited during the cycling. Fig.9 is the capacitive retention line. As we hope to characterize the electrochemical properties, we choose three electrodes test system. As electrolyte solution evaporates in long time cycling, the density change of solution effect electrochemical properties, we choose 1100times cycling. After 1100 times cycling, electrode capacitive retention is 92%; compared with normal metal oxids, it overcomes the dissolution problem of active material during cycling. A higher capacitive retention is a result by combination of two materials: CB provides porous 3D structure with high conductivity, improves the using rate of MnCO_3 active sites and provides transmission channel for electrons.

Fig.9. a) capacitive retention line of MnCO_3/CB and pure MnCO_3 at different scan rate; b) capacitive retention line of MnCO_3/CB composite at 100 mV/s for 1100 cycles.

4 Conclusions

1) Produced MnCO_3/CB composite under room temperature with liquid phase deposition method. XRD and SEM representation indicates that MnCO_3 disperse homogeneously formed in CB granules within the 3D structure.

2) Purified CB granules appear with no Reunion trend, contains massive negatively charged groups(carboxyl and quinonyl etc.) on its surface, which benefits CB granules dispersed homogeneously in solution to produce a homogeneous compound.

3) Electrochemical test shows: MnCO_3/CB composite has stable electrochemical properties and specific capacitance has double growth compared with pure MnCO_3 . Long time cycling capacitive retention reaches 92%. This research lays a foundation of further use for MnCO_3/CB composite in electrochemical field, and provides new ideas for the application of carbonate materials apply to supercapacitors.

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