Rational design of a 3D net-like carbon based Mn₃O₄ anode material with an enhanced lithium storage performance

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Abstract

An optimized structure design of three-dimensional (3D) net-like carbon based Mn_3O_4 (Mn_3O_4/CP) composite was realized based on the theory of explosive nucleation and in situ growth. Mn_3O_4/CP composite has been successfully prepared on a large scale with the filter paper adsorbed with manganese (II) oleate served as the raw materials by a facile thermal decomposition route. The obtained Mn_3O_4/CP composite shows a reversible capacity of 1005 mAh/g after 90 cycles at a current density of 100 mA g⁻¹, with a remarkably enhanced rate performance and an excellent cycling stability compared to the pure Mn_3O_4 nanostructure compared to the pure

Mn₃O₄ nanostructure which lose most of the capacity within 10 cycles. Even at the current density of 2000 mA/g, the specific capacity of Mn₃O₄/CP composite is still as high as 486 mAh/g, which is much higher than that of pure Mn₃O₄ (38 mAh/g) and the carbon materials (111 mAh/g). The enhancement of the electrochemical performance could be attributed to the synergy of Mn₃O₄ enwrapped with the 3D conductive carbon network, thus making it a promising anode material for large-scale energy storage applications. Moreover, this facile and effective synthetic strategy can be further explored as a universal approach for the rapid synthesis of other transition metal oxides and carbon hybrids with subtle structure engineering.

Key word: Mn₃O₄, filter paper, thermal decomposition, anode material, lithium storage performance

1. Introduction :

Rechargeable lithium-ion batteries (LIBs) have been extensively utilized as energy storage, while the power and energy density remain insufficient to satisfy the requirements of the fast developing electronic devices [1]. To meet the demands from these fast growing energy storage industries, the development of advanced anode materials with high energy density, and good rate capability replacing the commercial graphite anode materials is urgently required [2].

To date, transition metal oxides (TMOs), such as CoO, Co₃O₄, Fe₃O₄, SnO₂, NiO, Mn₃O₄ and MoO₂, have been regarded as potential anode of the LIBs because of the high theoretical specific capacity [3-5]. Among them, Mn_3O_4 has aroused much interest as the anode materials for its high theoretical capacity (about 937 mAh/g),

environmental benignity and excellent thermal stability [6]. As the anode material of the LIBs, the Mn_3O_4 nanoparticles have the advantages of shortening Li⁺ diffusion path, larger electrode/electrolyte contact area, higher rate performance and better cycle life [7]. However, the rapid oblique collapse of the electrode material structure of Mn_3O_4 during charge-discharge processes is caused by the huge volume change due to the large amount of metal Mn are produced and deposited around the Li₂O molecule, leading to fast capacity decay and poor rate performance. In addition, the agglomeration of metal particles and inherent low electrical conductivity of Mn_3O_4 during charging and discharging also results in poor cyclic performance. To address these issues, the introduction of carbon coating with Mn_3O_4 is considered as the most successful candidate being anode materials in LIBs. The nano-sized particles with a large specific surface area and confined dimension of Mn_3O_4 /carbon composite, which increase the electrochemical active sites and shorten the transport path of Li⁺ ion for enhanced kinetics, contribute to a high lithium-ion intercalation capacity [8].

On the whole, the introduction of carbon materials could significantly improve the electrical conductivity, prevent the agglomeration of metal particles, and maintain the stability of the structure of the electrode material as a mitigation layer for the volume change of the electrode material. The hybrids of Mn₃O₄ and various carbon composites have been reported for several previous works [9-12]. For the buffering matrix, one-dimensional carbon nanotubes are usually considered as a promising choice because of the excellent conductivity [13, 14]. Zhao *et al.* reported Mn₃O₄ with carbon nanotubes prepared by the solvothermal method and delivered a capacity of 592 mAh/g at a current density of 100 mA/g over 50 cycles [15]. Graphene has been widely used as conductive coating due to its remarkable conductivity and good mechanical flexibility [16, 17]. Graphene wrapped Mn₃O₄ nanoparticles were fabricated by a single-step hydrothermal method, which showed a high reversible specific capacity of 474 mAh/g at 100 mA/g upon 200 cycles [18]. Despite these progress, most of the preparation methods for micro/nanostructured Mn₃O₄/carbon composite are complicated and require tedious procedures and the improved electrochemical performance have been reported were not very satisfactory. It is still a challenge to develop a facile, efficient, and cost-effective method for preparing excellent high-performance nanostructured Mn₃O₄/carbon composite anodes for LIBs.

The new, cheap and readily available carbon materials have exhibited great potential used into composite electrodes. Filter paper is an outstanding source of nature carbon, which is abundant, low-cost in cellulose that promotes the generation of three-dimensional net-like structure [19]. According to the principle of minimum Gibbs free energy, namely, the surface free energy becomes higher with the decrease of particle size, particles tend to spontaneously coalesce and grow up together. In order to reduce surface energy and surface defects of the particles, the incorporation of 3D carbon materials can effectively prevent the mutual contact of nanoparticles, and provide enough extra space to inhibit the agglomeration and secondary growth of nanoparticles.

Herein, based on the theory of explosive nucleation and in situ growth, Mn₃O₄ nanoparticles were prepared by thermal decomposition and wrapped by 3D carbon

materials. In this article, for the first time, we have developed a green, simple and scalable method to realize the preparation of Mn₃O₄/CP composite as an excellent anode material for LIBs, which can be conveniently, rapidly and massively large scale produced. The resulting Mn₃O₄/CP composite, taking both of the advantages of nanosized structure and carbon hybridization, exhibited significantly enhanced cycling stability and rate performance as anode for LIBs. By comparing the electrochemical performances of three different samples (pure carbon materials, pure Mn₃O₄ and Mn₃O₄/CP composite), an insight into the comparable electrochemical performance related to the property of ion and electron transportation in the hybrid architecture was further obtained. We believe our work will endow some further efforts to maximize the available performance from this material in terms of high rate capacity and cycle performance for large-scale energy storage device.

2. Experimental

2.1 Preparation of Manganese (II) Oleate.

The manganese (II) oleate was prepared according to the previous report with some modification [20, 21]. Briefly, 11.52 g of manganese chloride tetrahydrate and 36.5 g of sodium oleate were dissolved in 80 g of deionized water. 60 g of ethanol and 140 g of hexane were added into the as-prepared solution. The resulting solution turned pink and a deep red after heated to 70 °C with a constant stirring for 8 h. The obtained solution was separated and the upper organic layer containing the manganese (II) oleate was washed several times with the warm deionized water in a separatory funnel. manganese (II) oleate was obtained after the rotary evaporation of hexane.

2.2 Synthesis of the Mn₃O₄/CP nanocomposite

Manganese oxide was synthesized by thermal decomposition of manganese (II) oleate in 1-octadecene at elevated temperatures [22]. Typically, 1.23 g of manganese (II) oleate, 0.28 g of oleic acid and 10 g 1-octadecene were added into a 50 mL threenecked round-bottomed flask with a stirring thoroughly at room temperature. Then, an appropriate amount of filter paper was immersed into the mixture after heated to 70 °C. The reaction mixture was degassed at 120 °C under vacuum for 1.5 h for removing any oxygen and moisture. The solution was heated to 300 °C with a heating rate of 3 °C/min and fixed to the temperature for 1 h under inert atmosphere. The asprepared solution was cooled to the room temperature. Subsequently, the filter paper was washed by the ethanol and isopropyl alcohol solutions for several times. The washed sample was dried at 80 °C for 5 h. The carbon and Mn₃O₄ nanocomposites were obtained after calcinated at 500 °C in a tubular furnace under Ar atmosphere, which was described as Mn₃O₄/CP. Additionally, the mixture without filter paper and the pure filter paper were calcinated at 500 °C with the same condition to obtain the pure Mn₃O₄ and carbon. The design and the preparing process of Mn₃O₄/CP composite is illustrated in Fig. 1, including three steps: 1) Filter paper is immersed in the Manganese (II) oleate. (2) The filter paper with metal oleate adsorbed on the surface is heated and decompose at high temperature in N₂ atmosphere. (3) Mn₃O₄/CP composite is obtained by the calcination of the thermal decomposition product.



Fig. 1. Schematic illustrations of the fabrication process of Mn₃O₄/CP composites.

2.3 Materials characterization

The crystalline phase of the Mn_3O_4/CP were examined by X-ray diffraction (XRD) on a X'Pert PRO MDP X-ray diffractometer with Cu K α radiation (λ =0.1542 nm) in the range of 10-80°. The morphologies were observed by field emission scanning electron microscopy (FESEM, Hitachi, SU8020), transmission electron microscopy (TEM, JEOL JEM-2100F). Element mapping was carried out using the energy-dispersive spectroscopy (EDS). The valence state of element and accurate elemental composition on the surface of the samples were analyzed by X-ray photoelectron spectrum (XPS, Thermo Fischer, ESCALAB 250 XI).

2.4 Electrochemical measurements

A homogeneous mixture consists of the active material, conductive carbon black (super-P-Li), and polyvinyl difluoride (PVDF) with a weight ratio of 7:2:1. The resultant slurry was spread on Cu foils after magnetic stirring for 24 h, dried in a vacuum oven at 60 °C for 12 h. The as-prepared Cu foils covered with the samples were cut into the pieces (a diameter of 12 mm) and weighed in a high-precision analytical balance. The batteries were assembled with pure Li foil as counter-electrode and reference electrode in a purity argon-filled glovebox. 1 M LiPF₆

dissolved in ethylene carbonate and diethyl carbonate (v/v=1:1) was used as the electrolyte. The discharge-charge testing was performed on Neware battery testing system after the cells were aged for 24 h. The cyclic voltammetry (CV) was carried out on an electrochemical workstation (Biologic) in a potential range of 0.01-3.0 V (vs Li⁺/Li) at a scan rate of 0.1 mV/s.

3. Results and discussion

The field-emission scanning electron microscopy (SEM) and the corresponding Energy dispersive X-ray spectroscopy (EDS) pattern in Fig. 2 demonstrate the general morphology of the Mn_3O_4 /CP composite. Fig. 2a-b shows that a large number of Mn_3O_4 nanoparticles on the surface of carbon substrate with homogeneous interspersion which can be further confirmed by the uniform distribution of the Mn, O and C elements shown in the EDX elemental mapping in Fig. 2c-g. The elements of Mn and O are homogeneously distributed on the carbon surface, and a certain quantity of C is observed.



Fig. 2. SEM and the corresponding EDS of Mn_3O_4/CP composite. (a)-(b) SEM

images, (c)-(f) element distribution, (g) EDS spectrum.

Transmission electron microscopy (TEM) is conducted to further display the morphology of Mn_3O_4/CP composite in more detail. As observed, the Mn_3O_4 nanoparticles are wrapped by the carbon materials. The average particle size of Mn_3O_4 was about 20-30 nm revealed by the TEM images. EDS is performed to uncover the element distribution and the general proportion (Fig. 3c-f). The HRTEM image of the Mn_3O_4/CP composite (Figure 2d) shows distinct lattice fringes spacing of 0.31 nm, which is in good agreement with the interplanar distances of (112) planes of Mn_3O_4 phase [23]. All of the results further confirm the Mn_3O_4 nanoparticles are anchored on the surface of the carbon substrate with excellent homogeneity and integrity.



Fig. 3. (a) TEM, (b) high-resolution TEM image, (c) HAADF-STEM images of Mn₃O₄/CP composites, (d)-(f) the corresponding elemental mappings of Mn, O and C

elements.

Fig. 4a depicts the XRD pattern of the Mn₃O₄/CP composite. Diffraction peaks are indexed to the phase of Mn₃O₄ with the corresponding JCPDS pattern PDF # 24-0734 (a = 5.765 and c = 9.472 Å) [24]. Diffraction peaks at 18.00° , 28.88° , 32.31° , 36.09°, 44.44°, and 59.840° are indexed to (101), (112), (103), (211), (220) and (224) planes of tetragonal Mn₃O₄. The narrow peaks with a high intensity indicate a good crystallization of Mn₃O₄. No peaks corresponding to the other manganese phase can be observed, demonstrating the formation of the pure Mn_3O_4 in the inert atmosphere. Amorphous carbon is observed at about 25° [25]. Raman experiments are extremely sensitive to the surface species and give out the responsive signals in the surface region because of the restricted penetration depth of the incident laser into the sample. In order to analyze the graphitization degree of the Mn₃O₄/CP composite, Raman spectrum is performed as shown in Fig. S1. The peak located at around 644 cm⁻¹ belongs to the characteristic peak of metal oxide (Mn-O) bond [26]. The peaks at about 1344 cm⁻¹ and 1595 cm⁻¹, respectively, corresponding to the D (defect) peak and G (Graphite) peak [27]. The defect and graphitization degree of the material can be judged by the intensity ratio between D peak and G peak (I_D/I_G) . The obtained $I_D/I_G=0.544$ suggests the higher level of graphitization is favorable to improve electrical conductivity and small degree of surface defect, thus be of benefit to facilitate the fluent stream of electrons, which makes it as a promising anode for LIBs [28].



Fig. 4. XRD pattern and XPS curves of Mn₃O₄/CP composite. (a) XRD pattern, (b) survey spectrum, (c)-(f) high-resolution of C 1s, O 1s, Mn 2p and Mn 3s.

To accurately analyze the element composition of the composite surface and the valence state of manganese, XPS spectra were collected in the binding energy ranging from 0 to 1200 eV. The C 1s at 284.8 eV was used as a calibration for the elements in the composites. A typical XPS survey of Mn_3O_4 /CP composite was shown in Fig. 4b, where Mn, O, and C elements were clearly detected, which could be attributed to the

in-situ growth of Mn₃O₄ nanoparticles on the carbon substrate. The C 1s XPS spectrum of Mn₃O₄/CP was also determined, as shown in Fig. 4c. A main peak centered at 284.7 eV was corresponding to the C-C bond configuration of the carbonization, while the peaks located at 286.5 and 285.3 eV were attributed to C-O and C=O bonds, respectively, relating with the surface functional groups [14, 29]. Fig. 4d depicted the XPS spectrum of Mn 2p, where Mn $2p_{1/2}$ peak and Mn $2p_{3/2}$ peak are located at 653.5 and 641.4 eV with a spin-energy separation of 11.7 eV, which agree well with the characteristic of Mn₃O₄ reported in the previous researches [30, 31]. In addition, Mn $2p_{3/2}$ peak can be well divided into the Mn⁴⁺ $2p_{3/2}$ part at 642.5 eV and $Mn^{2+} 2p_{3/2}$ part at 641.2 eV [32]. The O 1s spectra has been deconvoluted into two distinct independent peaks as shown in Fig. 4e, i.e., around 529.9 eV for the bonds of Mn-O and 532.2 eV for hydroxide resulting from the surface absorbed water [33]. The result confirmed the chemical states of the composites. The splitting energy of Mn 3s core-level was 5.45 eV (Fig. 4f), which was ascribed to the interaction between the other unpaired electrons in the d orbital and the remaining electrons in the 3s orbital [34]. The splitting width is agreement with the Mn_3O_4 XPS spectrum from the previous report [35].

Cyclic voltammetry (CV) experiment was conducted for further investigate the redox chemistries. The initial three CV curves for Mn_3O_4/CP composite measured in the voltage windows of 0.01-3V at a scan rate of 0.1 mVs⁻¹ were shown in Fig. 5a. The first CV curve is distinctly distinguishing with those in the successive cycles, suggesting that the reaction mechanism is different in the initial lithiation, which has

been already observed in the previous reported Mn_3O_4 based electrodes [36]. The Mn_3O_4 /CP anode undergoing a serial of electrochemical reactions can be explicated by the following equations [37, 38]:

$$Mn_{3}O_{4} + Li^{+} + e^{-} \rightarrow LiMn_{3}O_{4} \quad (1)$$
$$LiMn_{3}O_{4} + Li^{+} + e^{-} \rightarrow Li_{2}O + 3MnO \quad (2)$$
$$MnO_{x} + 2xLi^{+} + 2xe^{-} \leftrightarrow xLi_{2}O + Mn (x=1-1.5) \quad (3)$$

A broad reduction peak around 1.69 V in the first scan is assigned to the intercalation of Li^+ ions into Mn₃O₄ (equation 1). The peak at 1.46 V can be attributed to the conversion to MnO (equation 2). The irreversible reduction peak at 0.72 V is mainly corresponding to the generation of the solid electrolyte interface (SEI) resulting from the decomposition of the electrolyte on the surface of the electrode [39]. The sharp cathodic peak at 0.25 V corresponds to the reduction of MnO to metallic Mn. In the anodic sweep, three delithiation peaks at 1.28, 2.08, and 2.33 V are observed, indicating to the oxidation of Mn to Mn^{2+} and Mn^{2+} to the higher valance manganese accompanying by the decomposition of Li₂O [36, 40, 41]. However, the energy storage mechanism of Mn_3O_4 is dominated by the reversible conversion from MnO to metallic Mn (equation 3). In the second cycle, the reduction peak of Mn^{2+}/Mn^{0} at 0.25 V shifts to a higher station at 0.37 V, which is probably attributed to the improved kinetics due to the structural changes after the first cycle [29, 42]. The third CV curve mostly overlap with second one, suggesting the high reversibility of the electrochemical reactions of Mn₃O₄/CP composite during the subsequent cycles [43], therefore shows the remarkable capacity retention capability.

The voltage versus capacity profits of the 1st, 2nd, 3th, 5th, and 10th cycle of Mn₃O₄ and the Mn₃O₄/CP composites at a current density of 40 mA/g are exhibited in Fig. 5b. The characteristics of the charge-discharge curves are in good accordance with the conversion reaction of manganese oxide used as anode materials for the LIBs which have been reported before [44-47]. In the first discharge curve, one broad voltage plateau at 1.7~0.3 V is relate to the formation of the solid electrolyte interphase (SEI) layer and the initial reduction of Mn₃O₄ [48]. A well-defined discharge plateau at 0.3 V is corresponding to the reduction of MnO to metallic Mn [49]. The discharge plateau shifts to a higher voltage of 0.5 V in the second and the following cycles, which is consistent with the CV results. The Mn₃O₄/CP composite delivers a specific discharge capacity and a charge capacity of 1554 mAh/g and 927 mAh/g, respectively. The coulombic efficiency was 59.67%, which rose to 91.12% rapidly from the second cycle. The initial discharge capacities of Mn₃O₄/CP composite are higher than the theoretical capacity of Mn_3O_4 (937 mAh/g), which can be ascribed to the reversible growth of a polymeric gel-like film. The similar results have been revealed for the transitional metal oxides as the anode materials [25]. A sharp drop of Mn₃O₄/CP composite was observed in the second cycles, the irreversible capacity is relate to the formation of the complete SEI film and the irreversible reactions of Mn₃O₄ [50].

Fig. 5c presents the rate capability of CP, Mn_3O_4 or Mn_3O_4/CP composite at current densities ranging from 40 to 2000 mA/g. The average reversible discharge capacities of Mn_3O_4/CP composite are 1554, 772, 720, 650 and 580 mAh/g at the

current densities of 40, 100, 200, 500 and 1000 mA/g, respectively. The prepared Mn₃O₄/CP composite delivers a specific discharge capacity of 486 mAh/g even at the current density of 2000 mA/g, which is much higher compared with the theoretical specific capacity of the commercial graphite carbon (372 mAh/g). The average reversible discharge capacities of the pure Mn_3O_4 are 1650, 518, 440, 323, 181, 38, and 587 mAh/g at the current densities of 40, 100, 200, 500 1000, 2000 and 100 mA/g, respectively. A large first irreversible capacity and rapid capacity fade can be observed for pure Mn₃O₄. Comparing with Mn₃O₄, the reversibility of Mn₃O₄/CP composite is outstanding, which is related to the homogeneous dispersion of Mn₃O₄ nanoparticles on the carbon substrate. The introduction of 3D carbon provides an excellent electronic conductivity and a buffer the volume variation during the charge/discharge process. It is also worth noting that the discharge capacity can be recovered to around 98% of the initial capacity when the discharge current density is recycled back to 100mA/g from 2000mA/g, suggesting Mn₃O₄/CP composite possesses an excellent rates of charge/discharge and great electrochemical stability performances. After 10 cycles, the capacity of the material increases to 832 mAh/g. The remarkable rate performance of the Mn₃O₄/CP composite is superior to the pure Mn₃O₄, which is benefited from the unique structure of Mn₃O₄ coating on the conductive carbon substrate resulting in a significantly reduced path for the electron and ion diffusion. In addition, 3D carbon greatly improves the volume change and agglomeration of nanoparticles during the charging and discharging processes.



Fig. 5. Electrochemical performance of the prepared samples. (a) CV curves of Mn_3O_4/CP composites, (b) charge/discharge profiles of Mn_3O_4/CP composites at a current density of 40 mA/g, (c) rate performance at different current densities for Mn_3O_4 , CP, and Mn_3O_4/CP composites, (d) cycling performance of Mn_3O_4/CP composites.

The cycling stability of the Mn_3O_4/CP composites was evaluated by charging/discharging between 0.01-3 V at the current density of 100 mA/g (Fig. 5d). The Mn_3O_4/CP composites anode presents an excellent cycling stability without significant capacity decay except for the first two cycles. The capacity still maintains a capacity of 1005 mAh/g after the 90 cycles, compared to retention of 664 mAh/g by pure Mn_3O_4 electrode. The enhanced cycling performance can be attributed to the

introduction of the conductive carbon substrate as well, which acts both as a separator to restrain Mn_3O_4 nanoparticles from agglomeration and as a buffer to retard the volume change of nanoparticles [24]. The cycling performance of our material is superior to many similar materials in previous reports, the comparison between the asprepared Mn_3O_4/CP composite and the other analogous materials are listed in Table 1.

Sample	Reversible capacity	Cycles	Current density	Ref.
	(mAh/g)		(mA/g)	
Spongelike Mn ₃ O ₄	800	~30	100	[51]
Cu-doped Mn ₃ O ₄	400	100	100	[52]
Mn ₃ O ₄ -G	337	100	100	[53]
Mn ₃ O ₄	500	50	50	[54]
Graphene/ Mn ₃ O ₄	702	100	100	[32]
Mn ₃ O ₄ -graphene	500	60	100	[55]
Mn ₃ O ₄ -G	500	40	60	[56]
Mn ₃ O ₄ -G	573	100	100	[23]
G-mesoporous	600	93.7	100	[57]
Mn ₃ O ₄				
Mn ₃ O ₄ /CP	1005	90	100	This work

Table 1 Summary of the cycling performance of Mn₃O₄-related anodes

For a better understanding of the diffusion kinetics and the lithium-ion energy storage in the unique designed structure of Mn_3O_4/CP composites, electrochemical impedance spectroscopy (EIS) measurement was conducted. As illustrated in the Nyquist plots of the pure Mn_3O_4 and Mn_3O_4/CP composites (Fig 6), the intercept of

the high-frequency semicircle is related to the electrolyte resistance (R_s), the mediumfrequency semicircle equivalent to the charge-transfer resistance (R_{ct}), the lowfrequency slope of the line is attributed to the solid-state diffusion of Li⁺ ions through the lattice of the active material (Warburg resistance, R_w) [54, 58]. The diameter of semicircle for Mn₃O₄/CP composites is much smaller compared with that of pure Mn₃O₄ electrode, suggesting the enhanced conductivity and kinetic properties of Li⁺ ions [59], which is profited from the Mn₃O₄/CP unique designed structure, in which the incorporation of carbon improves the electrical conductivity as well as the smaller Mn₃O₄ nanoparticles with high specific surface area can sufficiently contact with the electrolyte [8]. Therefore, Mn₃O₄/CP composites is endowed the high rate capability and cyclic stability, excellent reversible capacity. In the low frequency, more vertical straight line of Mn₃O₄/CP composite than that of the pure Mn₃O₄, indicate the faster Li⁺ diffusion rate in the Mn₃O₄/CP electrodes [60].

To explored the Li-ion kinetics in Mn_3O_4/CP electrodes, CV curves are recorded at the scan rates of 0.1, 0.3, 0.5, 1 and 2 mV/s, respectively (Fig. 6b). The current increases with the increase of the scan rate of CVs. All the anodic peaks show a no significant shape change, but only a slight shift with the increase of scan rate. The obvious shifts of peak voltage are associate with the large polarization at the high scan rates [10]. The relationship between current (*i*) and the scan rates (*v*) which can qualitatively evaluate the degree of capacitive effect is described in equation (4) [61],

$$i = av^b$$
 (4)

where i represents the current, v represents the scan rate, a and b are constants. The

values of b can be deduced by the slop of the linear plots of log(v)-log(*i*), which are 0.81, 0.74 and 0.77 for the anodic (a and c) and cathodic (b) peaks (Fig. 6c). The results reveal that the performance of Li-ion storage in Mn₃O₄/CP composite stems from the mixed contributions of Li-ion diffusion and pseudocapacitive during the charge-discharge processes [62]. The ratio of the diffusion and capacitive contributions can be obtained by a quantitative calculation separating the current according to the equation (5) at the fixed potentials [12].

$$i(V) = k_1 v + k_2 v^{1/2} \qquad (5)$$

Where k_1v and $k_2v^{1/2}$ represent the capacitive and diffusion contributions, respectively. In which k_1 and k_2 values can be obtained from the slope and the intercept of the liner plots of $i(V)/v^{1/2}$ vs. $v^{1/2}$ [63]. As illustrated in Fig. 6d, the capacitive contribution for the Mn₃O₄/CP electrode is 38% at the scan rate of 0.1 mV/s, which demonstrates an increase behavior to 46, 58, 66 and 73% at the scan rates of 0.2, 0.5, 1. 0 and 2.0 mV/s, respectively. It indicates that the dominant pseudocapacitive contribution results in Mn₃O₄/CP the enhanced rate capability and superior cycle life.



Fig.6 (a) Nyquist plots of Mn_3O_4/CP and pure Mn_3O_4 , (b) CV curves at different scan rates, (c) Linear relationship between log(i) versus log(v), (d) Normalized contribution ratio of capacitive (black) and diffusion-controlled (red) capacities at different scan

rates

4. Conclusions

Based on the theory of explosive nucleation and in situ growth, a facile and scalable strategy is presented to prepare an excellent electrochemical performance Mn₃O₄/CP composites anode for LIBs. The Mn₃O₄/CP composites exhibited a good stability, with high reversible capacity retention and superior rate capability, which are attributed to the morphological evolution, in which Mn₃O₄ nanoparticles with an effective specific area provide the primary capacity. Meanwhile, 3D network carbon increases the conductivity and provides a rapid channel for the electrochemical reaction to alleviate the volume effect and could effectively prohibit the hybrid

nanoparticle aggregation. Last but not least, the interface built up from resultant network connection between Mn_3O_4 and carbon matrix can facilitate the pseudocapacitive which is fully testify by Li-ions kinetics analysis. This synthetic method proposed in this work may open up a new avenue to design and establish the hybrid structure for the other metallic oxide and carbon composite.

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