MoO$_2$/Mo$_2$C/C spheres as anode materials for lithium ion batteries

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A B S T R A C T

MoO$_2$/Mo$_2$C/C spheres have been synthesized through hydrothermal and calcination processes. MoO$_2$ is well known for its high theoretical capacity of 838 mAh g$^{-1}$, but undergoes capacity fading during Li$^+$ insertion/extraction processes. Mo$_2$C has high specific conductance (1.02 × 10$^8$ S cm$^{-1}$) that can provide better electronic conductivity. Carbon is popular for its ability to accommodate the volume variation during charge/discharge. By taking advantage of the combination of Mo$_2$C and C, these MoO$_2$/Mo$_2$C/C spheres demonstrate not only high cycling performance, but also good rate capability when they are used as anode materials for lithium ion batteries. After 100 cycles at 100 mA g$^{-1}$, the discharge capacities of the MoO$_2$/Mo$_2$C/C spheres remain at 800 mAh g$^{-1}$, suggesting that MoO$_2$/Mo$_2$C/C spheres are promising candidates as anode material for lithium ion batteries.

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1. Introduction

To date, transition metal oxides, such as iron oxide, nickel oxide, and cobalt oxide, have been widely studied as candidate anode materials for lithium ion batteries (LIBs) due to their ability to react with more than two Li$^+$ ions per formula unit, resulting in higher capacity than that of graphite [1–6]. Molybdenum dioxide (MoO$_2$), one of the transition metal oxides, is remarkably attractive as a host material for lithium ion storage. Its rich chemistry associated with many valence states, low cost, low electrical resistivity, and great electrochemical activity towards lithium are the ideal properties for LIB application [7–9]. In terms of capacity, MoO$_2$ has a high theoretical capacity of 838 mAh g$^{-1}$, due to its ability to accommodate 4 lithium ions per formula unit [10].

In spite of its advantageous properties, MoO$_2$ suffers from two drawbacks. Firstly, the redox conversion process of bulk MoO$_2$ is extremely limited due to the sluggish kinetics of lithium ion insertion [11,12]. Secondly, large volume variations take place in the Li$^+$ insertion/extraction processes, leading to electrical pathway damage, disintegration of the active material from the current collector, and serious capacity fading [7,8,11,13–16].

Nanostructuring and fabricating MoO$_2$–carbon composites have been considered in order to enhance the cycling performance of MoO$_2$ electrode. Nanostructuring can maximize the contact surface area between the electrode and electrolyte, so that the diffusion paths for electrons and lithium ions become shorter, resulting in high capacity and rate performance. The nanostructured material still suffers, however, from volume change during lithiation/delithiation.

The other strategy, forming a carbon composite, has demonstrated its ability to improve the performance of MoO$_2$ electrode [7,17–20]. Carbon acts not only to prevent exfoliation of the active material, but also to improve the conductivity of MoO$_2$, resulting in the enhancement of charge–discharge reversibility and cycling performance. MoO$_2$/graphene oxide (GO) composite delivered a capacity of 720 mAh g$^{-1}$ and 560 mAh g$^{-1}$ after 30 cycles at a current density of 100 mA g$^{-1}$ and 800 mA g$^{-1}$, respectively [10]. MoO$_2$–ordered mesoporous carbon could maintain a capacity as high as 689 mA h g$^{-1}$ after 50 cycles at 50 mA g$^{-1}$ [21]. MoO$_2$–C spheres exhibited good cycling performance and delivered a...
discharge capacity of 812 mAh g\(^{-1}\) when cycled at 0.2 A g\(^{-1}\) [9]. MoO\(_2\)–carbon hybrid nanowires delivered a capacity of 327 mAh g\(^{-1}\) at a current density of 1 A g\(^{-1}\) after 20 cycles [22].

Recently, a new approach to modifying MoO\(_2\) material was studied by Zhang et al. [23]. They used Mo\(_2\)C to improve the performance of the MoO\(_2\) by taking advantage of its high specific conductance (1.02 \(\times 10^2\) S cm\(^{-1}\)) and electrochemical inactivity. The high specific conductance of Mo\(_2\)C minimizes the charge transport resistance, leading to better electronic conductivity, and the electrochemical inactivity improves structural stability [24,25]. Moreover, Gao et al. synthesized Mo\(_2\)C–C hybrid nanospheres through solvothermal synthesis and a reduction-carbonization method, and they demonstrated capacity of 672.7 mAh g\(^{-1}\) after 50 cycles at a current density of 100 mA g\(^{-1}\) [26].

In this work, we have combined the advantages of both Mo\(_2\)C and C in order to improve the performance of MoO\(_2\) by preparing MoO\(_2\)/Mo\(_2\)C/C spheres as anode material for lithium-ion batteries by the hydrothermal method followed by calcination. The as-prepared MoO\(_2\)/Mo\(_2\)C/C spheres have demonstrated not only high cycling performance, with capacity of 800 mAh g\(^{-1}\) after 100 cycles, but also good rate capability. The excellent electrochemical performance can be ascribed to the synergetic effects of Mo\(_2\)C, carbon, and MoO\(_2\) in the composite anode material.

2. Experimental

2.1. Preparation of materials

First, the resol precursor was made by mixing and stirring 0.6 g phenol, 2.1 ml formalin aqueous solution (37 wt %) and 15 ml NaOH aqueous solution (0.1 M) at 70 °C for 0.5 h. After that, 0.96 g Pluronic F127 triblock copolymer (Sigma Aldrich) dissolved in 15 ml H\(_2\)O was added. Then, the stirring was continued for 2 h at 66 °C. After that, 50 ml water was added to dilute the solution, and stirring was continued for 18 h. The obtained solution was designated as the Pluronic F127–resol mixture solution. Afterwards, 17 ml of the obtained solution, 10 ml ethylene glycol, X mmol (X = 0.5, 0.25) ammonium heptamolybdate tetrahydrate (AHM), and 41 ml H\(_2\)O were mixed and stirred for 1 h. The solution was moved into an autoclave and heated at 180 °C for 24 h. The obtained products were collected by centrifuge, washed with deionized water and ethanol, and dried at room temperature. The sample was further annealed at 700 °C for 4 h in nitrogen atmosphere with a heating rate of 2 °C/min. The resultant samples obtained from 0.5 to 0.25 mmol (NH\(_4\))\(_6\)Mo\(_7\)O\(_{24}\) 4H\(_2\)O were denoted as MMC-050 and MMC-025, respectively. For comparison purposes, molybdenum dioxide nanoparticles (denoted as MoO\(_2\) np) were prepared by the same procedure as MMC-050 and MMC-025 without using the Pluronic F127–resol mixture solution.

2.2. Material characterisation

The crystal structure of the materials was characterised by X-ray diffraction (XRD; GBC MMA Diffractometer, Cu K\(_\alpha\), \(\lambda = 1.5406\) Å) and small-angle X-ray scattering (SAXS) with a Nanostar U small-angle X-ray scattering system (Bruker, Germany) using Cu K\(_\alpha\) radiation. The dimensions and morphology were measured using field emission scanning electron microscopy (FESEM; JEOL JSM-7500) and transmission electron microscopy TEM; JEOL, 2011). Thermogravimetric analysis (TGA; Mettler Toledo TGA/DSC1) was used to determine the carbon content. The specific surface area was measured using the Brunauer–Emmett–Teller (BET) method.

For electrochemical performance testing, working electrodes were prepared by mixing 85 wt % sample as the active material, 6 wt % conductive agent (carbon black, Super-P-Li), and 9 wt % polyvinylidene difluoride (PVDF) binder, and the resultant slurry was pasted uniformly onto copper foil. The as-prepared working electrodes were then dried in a vacuum oven at 120 °C for 12 h. Electrochemical cells (CR2032 coin type) were assembled in an Ar-filled glove box (Mbraun, Unilab, USA) by using the working electrode, a separator (polypropylene film), Li foil as the reference and counter electrode, and 1 M LiPF\(_6\) in a 1:1 (v/v) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) as the electrolyte. The cells were galvanostatically charged and discharged over the voltage range of 0.01–3 V vs Li/Li\(^+\) at different constant current densities, based on the weight of the sample, on a Land CT2001A cycler.

3. Results and discussion

A schematic illustration of the fabrication of the MoO\(_2\)/Mo\(_2\)C/carbon spheres is presented in Fig. 1. Resol–F127 composite is produced by the interaction between the resol precursor and the triblock copolymer Pluronic F127 under stirring at a temperature of 66 °C for 18 h. After that, the composite interacts with AHM and ethylene glycol under the hydrothermal process at 180 °C for 24 h. In this process, the MoO\(_2\)/resin sphere precursor is formed. The MoO\(_2\)/resin sphere precursor is the product of the reduction of AHM with ethylene glycol. The calcination process at a temperature of 700 °C in N\(_2\) leads to the formation of porous spheres of carbon and MoO\(_2\). Further reaction of the MoO\(_2\) and the carbon generates Mo\(_2\)C, resulting in the MoO\(_2\)/Mo\(_2\)C/carbon spheres.

XRD patterns of the MoO\(_2\)/Mo\(_2\)C/carbon sphere composites and MoO\(_2\) nanoparticles are shown in Fig. 2(a). The patterns show a combination of peaks belonging to MoO\(_2\) and Mo\(_2\)C in both the MMC-050 and the MMC-025 samples. The diffraction patterns can be indexed to monoclinic MoO\(_2\) with space group P2\(_1\)/c (JCPDS 78-1071) and orthorhombic Mo\(_2\)C with space group Pca21 (JCPDS 77-0720). The diffraction peaks located at 25.9°, 36.9°, 53°, and 53.3° belong to the (011), (200), (312), and (022) planes of MoO\(_2\), respectively. The peaks located at 34.5°, 39.5°, 61.7°, 69.7°, and 74.6° are assigned to the molybdenum carbide (Mo\(_2\)C). No diffraction peaks corresponding to other Mo species were observed, suggesting that all of the AHM was transformed into MoO\(_2\) and Mo\(_2\)C species. Table 1 lists the compositions of MMC-050 and MMC-025 from the thermogravimetric analysis (TGA) data in Fig. 5 (Supporting Information) and Match! software analysis of XRD peaks.

Nitrogen adsorption–desorption isotherms of the MMC-050 and MMC-025 are presented in Fig. 2(b). The Figure shows type IV curves according to the IUPAC classification, suggesting mesoporous material, and it displays typical H1 hysteresis loops, which are usually found in spherical structures. The mesostructure has been confirmed by SAXS analysis. The SAXS patterns of MMC-050 and MMC-025 in Fig. 52 in the Supporting Information show no peaks, indicating disordered mesostructure. The pore distribution curves (inset in Fig. 2(b)) reveal that MMC-050 and MMC-025 have porous structure. The disordered porous structure could be generated by the phase separation process in F127 micelles after surfactant removal during the self-assembly process. MMC-050 and MMC-025 have BET surface areas of 154.3 m\(^2\) g\(^{-1}\) and 159.6 m\(^2\) g\(^{-1}\), respectively. The total pore volume of MMC-050 is 0.26 cm\(^3\) g\(^{-1}\), while MMC-025 has a total pore volume of 0.15 cm\(^3\) g\(^{-1}\).

The morphological and textural details of the samples were revealed by SEM and TEM. Fig. 3 displays SEM images of the MMC-050 and MMC-025 samples, while an SEM image of the MoO\(_2\) nanoparticles can be seen in Fig. S3 (Supporting Information). Fig. 3(a–d) gives the general morphology of the MMC-050 and MMC-025 samples. As can be seen in Fig. 3(b, d), the size distribution ranges of the MMC-050 and the MMC-025 spheres are
between 2–3 and 1–3 μm, respectively. The surface appearance of MMC-025 is smoother than that of MMC-050. The smoother appearance of MMC-025 may be due to the use of a lower concentration of precursor, leading to the presence of a smaller amount of Mo species compared to MMC-050. In order to see the distribution of Mo species (MoO₂ and Mo₂C), energy dispersive X-ray spectroscopy (EDS) mapping was performed on MMC-025, as shown in Fig. 3(e–g), which confirms that the molybdenum and carbon are uniformly distributed in the carbon spheres. Fig. 4 presents SEM images of the MMC-025 (Fig. 4(a)) and MMC-050 (Fig. 4(b)) samples after cycling performance testing. It can be seen that both MMC-025 and MMC-050 can maintain their spherical morphology after the cycling performance test, showing the stability of the structure.

TEM and high resolution TEM (HR-TEM) images of the MMC-025 sphere composite are shown in Fig. 5. Fig. 5(a) shows the appearance of a sphere at low resolution. The positions of MoO₂ and Mo₂C in the spheres cannot be identified clearly because they overlap with each other, as confirmed by EDS mapping in Fig. 5(e–g). An HRTEM image of the sample is displayed in Fig. 5(b). The HRTEM observations demonstrate that the spheres are composed of both MoO₂ and Mo₂C nanoparticles. The 2.28 and 2.42 Å lattice fringes are associated with the (211) planes of Mo₂C and the (200) planes of MoO₂, respectively. The results are in good agreement with the XRD analysis. The corresponding selected area electron diffraction (SAED) pattern is shown in Fig. 5(c), where the rings can be indexed to monoclinic MoO₂ and orthorhombic Mo₂C, which are also consistent with the XRD results.

Representative charge–discharge profiles of MMC-050 at a current density of 100 mA g⁻¹ in a voltage window of 0.01–3 V are shown in Fig. 6(a). The first discharge and charge capacities of the MoO₂/Mo₂C/carbon spheres are approximately 1172 and 790.3 mAh g⁻¹, respectively, calculated based on the total weight of the composite material. The corresponding coulombic efficiency is 67.4% for the first cycle. The capacity loss in the first cycle is attributed to irreversible processes affected by three factors: the trapping of some lithium ions in the MoO₂ lattice, the formation of a solid electrolyte interphase (SEI) layer, and electrolyte molecule decomposition. No significant capacity fading is observed in the following 2nd, 20th, and 50th cycles. The appearance of Mo₂C and C in the composite spheres can increase the structural stability and buffer the volume changes during insertion/extraction of lithium ions as well, and as a result, there is no serious capacity fading after 50 cycles.

The cycling performances of MMC-050, MMC-025, and MoO₂ nanoparticles at a current density of 100 mA g⁻¹ over a voltage range of 0.01–3 V are displayed in Fig. 6(b). Both samples of MoO₂/Mo₂C/carbon spheres (MMC-050 and MMC-025) show not only improved discharge capacities compared to the MoO₂ nanoparticles, but also show higher discharge capacities than their theoretical capacities, which are 466.39 and 412.33 mAh g⁻¹ for

<table>
<thead>
<tr>
<th>Sample</th>
<th>C (%)</th>
<th>MoO₂ (%)</th>
<th>Mo₂C (%)</th>
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<tr>
<td>MMC-050</td>
<td>10</td>
<td>35.1</td>
<td>54.9</td>
</tr>
<tr>
<td>MMC-025</td>
<td>20</td>
<td>23.84</td>
<td>56.16</td>
</tr>
</tbody>
</table>
MMC-050 and MMC-025, respectively (details are available in the Supporting Information). When those MoO$_2$/Mo$_2$C/carbon spheres are charged and discharged, the discharge capacities are fairly stable for the first 20 cycles. These stable discharge capacities are better than those of MoO$_2$/carbon spheres and MoO$_2$/Mo$_2$C heteronanotubes, which undergo significant capacity fading in the initial
cycles \[9,23\]. The stable discharge capacities of the MoO₂/Mo₂C/
carbon spheres indicate that the combination of Mo₂C and C in the
spheres has significant advantages for the cycling performance of
MoO₂ by preventing the capacity from declining in the initial cycles.
More importantly, the discharge capacities of MMC-050 and MMC-
025 are well maintained around 800 mAh g\(^{-1}\) after 100 cycles. The

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**Fig. 5.** (a) TEM image of MMC-025 sphere at low resolution; (b) higher magnification TEM image of the selected area of MMC-025 in (a); (c) SAED pattern of (a); (d–g) EDS mapping of selected area in (a). (A color version of this figure can be viewed online.)

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**Fig. 6.** (a) Charge/discharge voltage profiles of MMC-050 at the current density of 100 mA g\(^{-1}\) for the selected cycles indicated (inset: charge/discharge profiles of MoO₂ nanoparticles); (b) cycling performances of MMC-050, MMC-025, and MoO₂ np in the voltage range of 0.01–3 V at the current density of 100 mA g\(^{-1}\); (c) cycling performances of MMC-050, MMC-02, and MoO₂ np at higher current density (500 mA g\(^{-1}\)); (d) rate capability of MMC-050, MMC-025, and MoO₂ np at various current densities. (Note: The discharge capacity is used in the (b), (c), and (d)). (A color version of this figure can be viewed online.)
cycling performance of the MoO2/Mo2C/C electrodes is also significantly higher than that of the MoO2 nanoparticles. The superior cycling performance of the MoO2/Mo2C/C0.5 carbon spheres can be attributed to its structure and configuration, consisting of porous spheres, the good electrical conductivity of carbon and Mo2C in the composite, the buffering effect of carbon, which accommodates and alleviates the volume changes of MoO2 during cycling and the structural stability of Mo2C [9,22,23,26–36]. MoO2, Mo2C, and carbon work simultaneously and synergistically, resulting in the superior cycling performance of the MoO2/Mo2C/C0.5 carbon spheres.

The electrochemical performance, especially the rate capability of MMC-050 and MMC-025 are superior to the discharge capacities of reported MoO2, MoO2/Mo2C/C0.5 hybrid, and MoO2/C0.5 carbon composite, as shown in Table 2 [9,23,26,37,38]. The cycling performances of the present MoO2/Mo2C/C0.5 carbon sphere and MoO2/C0.5 nanospheres electrodes have also been studied at higher current densities (500 mA g\(^{-1}\)), as shown in Fig. 6(c). The cells delivered discharge capacities of 650 and 550 mAh g\(^{-1}\) after 100 cycles for MMC-050 and MMC-025, respectively, and showed better performance than the cells containing MoO2 nanoparticles.

The MoO2/Mo2C/C0.5 nanospheres samples also exhibit excellent rate capability (Fig. 6(d)). The MMC-050 and MMC-025 samples show higher capacities than the MoO2 np at all current densities. The capacity decrease in the initial cycle for MMC-050 and MMC-025 is related to irreversible processes involving three factors: some lithium ions that are trapped in the MoO2 lattice, the formation of a solid electrolyte interphase (SEI) layer, and decomposition of electrolyte molecules. The initial coulombic efficiency of MMC-050 and MMC-025 is 79.2% and 65.1%, respectively, and the difference may due to the different composition, i.e. different ratio of MoO2, Mo2C, and carbon in the composites. The discharge capacities of MMC-050 are 880, 750, and 680 mAh g\(^{-1}\) at current densities of 100, 250, and 500 mA g\(^{-1}\), respectively. In contrast, the MoO2 np shows lower capacities of 600, 550, and 400 mAh g\(^{-1}\) at current densities of 100, 250, and 500 mA g\(^{-1}\), respectively. The capacities of MMC-050 and MMC-025 remain as high as the initial capacities when the current density is returned to 100 mA g\(^{-1}\) after deep cycling at 5 A g\(^{-1}\). Our MoO2/Mo2C/C0.5 composite anode materials exhibit better rate capability compared with those of MoO2/C0.5 carbon and Mo2C/C0.5 composite anodes reported in the literatures [10,21,26,39,40]. The superior rate capability of MoO2/Mo2C/C0.5 carbon spheres can be explained by the following reason. Firstly, the porous carbon spheres provide short pathways for the transport of electrons and also supply the space for the volume changes of MoO2. Secondly, the good contact of MoO2 nanoparticles, Mo2C/C0.5 nanospheres, and the carbon in the spheres reduces the electrode resistance, thereby facilitating electron movement. The appearance of Mo2C also enhances the electronic conductivity of the spheres, generating the good rate capability performance.

Cyclic voltammetry (CV) of MMC-025 was conducted to inspect the redox behaviour of the sample during charging–discharging. Fig. 7(a) shows a cyclic voltammogram of MMC-025 at a scan rate of 0.1 mV s\(^{-1}\) over the potential range of 0.01–3.0 V. When the potential is above 1.0 V, the lithium ions are inserted into the MoO2 structure, resulting in Li1.5MoO2, and when discharge is lower than 1.0 V, Li0.5MoO2 is gradually transformed into Li2O and Mo metal. The first cycle displays an irreversible peak at 0.7 V, which is related to decomposition of electrolyte and solid electrolyte interphase (SEI) formation. Two reduction/oxidation pairs at 1.24/1.4 V and 1.52/1.7 V were observed in the following cycles and are correlated with the reversible phase transitions of partially lithiated Li1.5MoO2 during charging/discharging [41]. Meanwhile, two pairs of peaks from MoO2 nanoparticles can be observed at 1.27/1.5 V and 1.52/1.7 V in the inset in Fig. 7(a). The CV curves are stable after the second cycle, with all the cycles repeating themselves very well, indicating that the phase transitions are highly reversible and demonstrating the advantages of Mo2C and C for the structural stability of MoO2.

Electrochemical impedance spectroscopy (EIS) measurements were performed in order to understand the kinetic process. Fig. 7(b) shows the Nyquist plots of the MMC-050, MMC-025, and MoO2 np samples after 10 cycles. All plots show a semicircle in the high frequency region related to the charge transfer and ionic resistances and an inclined line at low frequencies, which is associated with the ion diffusion within the anode. The semicircles for MMC-050 and MMC-025 were smaller than that of MoO2 np, which is reasonable because the Mo2C and carbon can promote electron transfer from embedded MoO2 nanoparticles and thus increase conductivity. Also, the unique architecture of the porous spheres facilitates immersion of the porous spheres in the electrolyte, thus shortening the pathways for lithium ion diffusion. The effect of Mo2C on the samples can also explained by calculating the lithium diffusion coefficient from EIS data using the following equation

\[ D = R^2T^2/2A^2n^4F^2C^2\sigma^2 \]  

where \( D \) is the diffusion coefficient of lithium ions (cm\(^2\) s\(^{-1}\)) [42], \( R \) is universal gas constant, \( T \) means the absolute temperature, \( A \) is the area of the cathode (cm\(^2\)), \( n \) is the number of electrons involved, \( F \) is the Faraday constant, \( C \) is the concentration of lithium ions, and \( \sigma \) is the Warburg factor, which is related to \( Z_{re} \), \( \sigma \) is obtained from the slope of the lines in Fig. 8.

\[ Z_{re} = R_l + R_{ct} + \sigma \omega^{-1/2} \]  

The calculated lithium ion diffusion coefficients are 5.89 \times 10^{-19} cm\(^2\) s\(^{-1}\), 3.18 \times 10^{-15} cm\(^2\) s\(^{-1}\), and 4.97 \times 10^{-15} cm\(^2\) s\(^{-1}\) for MoO2 np, MMC-025, and MMC-050, respectively. The diffusion

**Table 2** Comparison of the electrochemical performance of MMC-050 with some published reports on MoO2 and MoO2/C0.5 carbon composites.

<table>
<thead>
<tr>
<th>Electrode description</th>
<th>Rate capability</th>
<th>Specific capacity after 100 cycles</th>
<th>Reference</th>
</tr>
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<tbody>
<tr>
<td>Hierarchical MoO2 monolith</td>
<td>Not available</td>
<td>719 mAh g(^{-1}) at 200 mA g(^{-1}) (after 20 cycles)</td>
<td>[37]</td>
</tr>
<tr>
<td>MoO2/C</td>
<td>500 mAh g(^{-1}) at 400 mAh g(^{-1})</td>
<td>500 mAh g(^{-1}) at 100 mA g(^{-1})</td>
<td>[38]</td>
</tr>
<tr>
<td>MoO2/C spheres</td>
<td>375 mAh g(^{-1}) at 1.2 A g(^{-1})</td>
<td>800 mAh g(^{-1}) at 200 mA g(^{-1})</td>
<td>[9]</td>
</tr>
<tr>
<td>MoO2/Mo2C heteronanotubes</td>
<td>350 mAh g(^{-1}) at 500 mA g(^{-1})</td>
<td>800 mAh g(^{-1}) at 200 mA g(^{-1})</td>
<td>[23]</td>
</tr>
<tr>
<td>Mo2C/C nanospheres</td>
<td>300 mAh g(^{-1}) at 1 A g(^{-1})</td>
<td>673 mAh g(^{-1}) at 100 mA g(^{-1}) (after 50 cycles)</td>
<td>[26]</td>
</tr>
<tr>
<td>This work (MMC-050)</td>
<td>400 mAh g(^{-1}) at 1 A g(^{-1})</td>
<td>800 mAh g(^{-1}) at 100 mA g(^{-1})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>700 mAh g(^{-1}) at 500 mA g(^{-1})</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>600 mAh g(^{-1}) at 1 A g(^{-1})</td>
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coefficients of MMC-025 and MMC-050 are much higher than the diffusion coefficient of MoO2 np. It is evident that Mo2C helps to reduce the charge transfer resistance, which leads to better electronic conductivity and ultimately increases lithium ion diffusion in MMC-025 and MMC-050.

4. Conclusions

In summary, we have successfully fabricated MoO2/Mo2C/C spheres through hydrothermal and calcination processes. After 100 cycles, the discharge capacities of MMC-050 and MMC-025 are well maintained at over 800 mAh g\(^{-1}\). The MoO2/Mo2C/Carbonate samples also demonstrate better rate capability compared to MoO2 nanoparticles, MoO2/carbon, MoO2/Mo2C, and Mo2C/C composites. The structure of these samples with their porous carbon-containing spheres, the good electrical conductivity of carbon and Mo2C in the composite, and the buffering effect of carbon can accommodate and alleviate the volume changes throughout the cycling process. The good rate capability performance is generated by three factors: the porous carbon spheres provide short pathways for the transport of electrons and also supply the space for the volume changes of MoO2, the good contact of MoO2 nanoparticles, Mo2C nanoparticles, and the carbon in the spheres reduces the electrode resistance, thereby facilitating electron movement and also provide short pathways for the transport of electrons, and Mo2C with its high specific conductance enhances the electronic conductivity of the spheres and also maintains the structural stability of the spheres during cycling. MoO2, Mo2C, and carbon work simultaneously and synergistically, resulting in the superior cycling performance and good rate capability of the MoO2/Mo2C/carbon spheres. By combining the advantages of MoO2, Mo2C, and carbon, the MoO2/Mo2C/carbon spheres could be a promising anode material for lithium ion batteries.

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Appendix A. Supporting information

Supporting information related to this article can be found at http://dx.doi.org/10.1016/j.carbon.2015.10.076.

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