Mixed Molybdenum Oxides with Superior Performances as an Advanced Anode Material for Lithium-Ion Batteries

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A simple and effective carbon-free strategy is carried out to prepare mixed molybdenum oxides as an advanced anode material for lithium-ion batteries. The new material shows a high specific capacity up to 930.6 mAh·g⁻¹, long cycle-life (>200 cycles) and high rate capability. 1D and 2D solid-state NMR, as well as XRD data on lithiated sample (after discharge) show that the material is associated with both insertion/extraction and conversion reaction mechanisms for lithium storage. The well mixed molybdenum oxides at the microscale and the involvement of both mechanisms are considered as the key to the better electrochemical properties. The strategy can be applied to other transition metal oxides to enhance their performance as electrode materials.

As one of the solutions for our new energy-based economy, lithium ion batteries are widely used in mobile devices, such as cellular phones and laptops, because of their relatively high volumetric and gravimetric energy density1,2. However, in order to meet the requirements for applications in electric vehicles, safe electrode materials with less cost, higher energy density, better rate performance and longer service life need to be designed3. Transition-metal oxides, which often have much higher theoretical capacity than traditional graphite materials, have been extensively studied as the anode materials for lithium ion batteries4. Molybdenum oxides (including both MoO₂ and MoO₃) represent attractive candidates due to their high theoretical capacity (about 838 mAh·g⁻¹ for dioxides and 1117 mAh·g⁻¹ for trioxides). Bulk molybdenum oxides, however, show much lower capacities compared with their theoretical ones, which can be attributed to the significant volume change during the charge and discharge processes and the intrinsic slow kinetics for the conversion reactions5.

Recently, metal oxide nanostuctures, especially nanostructured oxides have been prepared as anode materials for lithium ion batteries due to their short diffusion length, larger reaction surface area between the electrode and electrolyte, as well as extra space for better accommodation of the strain induced by large volume changes6–11. For example, molybdenum dioxide with a yolk-shell structure achieves a discharge capacity of 847.5 mAh·g⁻¹ after 50 cycles at 50 mA·g⁻¹12. Uniform carbon coated nanospheres exhibit a discharge capacity of 410 mAh·g⁻¹ after 30 cycles even at 3 C rate6. Coating highly conductive materials, such as carbon, is another strategy to improve the performances of metal oxides by increasing the electrode conductivity, as well as possibly improving the surface chemistry of the active material. The MoO₂ hollow structures coated with Mo₂N show a capacity of 815 mAh·g⁻¹ after 100 cycles at 100 mA·g⁻¹13. Nevertheless, it is usually expensive to prepare the complex nanostructure and the capacity fading often occurs during the cycling process, while coating conductive materials with low capacity reduces the specific capacity of the active materials.

Partial oxidation or reduction strategy has been employed to improve the electrochemical properties of cathode materials, for example, controlled reduction of LiV₃O₈ generate Li₅V₂O₈/LiV₂O₄ composite with significantly improved cycling performances and rate capability14. Herein we report a very simple and convenient method to prepare the mixed molybdenum oxides (MMO, MoOₓ, 2 < x < 3) by moderately oxidizing molybdenum dioxide nanoparticles under mild oxidizing atmosphere. The obtained MMO exhibits a discharge capacity as high as 930.6 mAh·g⁻¹ at a current density of 200 mA·g⁻¹ after 200 cycles as an advanced material, indicating this material has potential for applications in lithium-ion batteries.

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Experimental Section
Preparation of the MoO\textsubscript{2} nanoparticles. MoO\textsubscript{2} nanoparticles were prepared by using a hydrothermal method reported by Liu et al.\textsuperscript{15}. In a typical experiment, 1 g of ammonium heptamolybdate tetrahydrate was dissolved into the mixed solvent of 45 mL distilled water and 5 mL ethylene glycol (EG). After that, the mixture was transferred into a 100 mL Teflon-lined stainless-steel autoclave and was kept in an oven at a temperature of 180 °C for 48 h. The resulted black precipitate was centrifuged, and then washed by distilled water and followed by ethanol for three times. The product was finally dried at the 80 °C.

Preparation of the MMO and MoO\textsubscript{3} nanoparticles. To prepare MMO, the as prepared MoO\textsubscript{2} nanostructured powders was heated in a tube furnace at a rate of 5 °C·min\textsuperscript{−1} to 500 °C and kept at the temperature for 100 min. A mixed gas containing a small fraction of oxygen in nitrogen was flowed into the system at a rate of 20 mL/min. The fractions of oxygen were controlled as 0.2% and 1%, in order to achieve the final product MMO and MoO\textsubscript{3}, respectively.

Materials Characterization. The XRD patterns were acquired with an X-ray diffractometer (Philips Analytical X’pert Pro) at a 2θ range of 10–70°. The diffractometer was equipped with a Cu Kα radiation (λ = 1.5418 Å) and operated at 40 kV and 40 mA. The air sensitive samples were protected by Kapton films in the XRD measurement. The morphology of the samples were investigated using a field-emission scanning electron microscope (Hitachi FE-SEM S4800). X-ray photoelectron spectroscopy (XPS) was used to survey the surface compositions and the chemical states of the samples (PHI5000 VersaProbe, PerkinElmer). The hydrocarbon C 1 s peak at 284.5 eV was chosen as the reference for the binding energies. The XPS spectra were analyzed with the software XPSPeak 4.1. The ratio of the peak area of the Mo 3d\textsubscript{5/2} peak to the Mo 3d\textsubscript{3/2} peak is fixed to 1.5 while the binding energy separation is set to 3.0 eV. A Bruker Advance III 400 MHz spectrometer with a 3.2 mm Magic Angle Spinning (MAS) probe was used for acquiring the \textsuperscript{7}Li solid-state NMR spectra at a resonant frequency of 155.46 MHz. A spin-echo and a 2D exchanged pulse sequence were used in the data acquisition. In order to select the intensity of the resonance due to the SEI, a T\textsubscript{2} filter was used in the spin-echo NMR data acquisition. After discharging to $5 \times 10^{-3}$ V, the self-supported electrode\textsuperscript{16} was taken out, rinsed with dimethyl carbonate (DMC) to remove the residual electrolyte, before it was dried and packed into NMR rotors in an Ar glove box, and spun at 18 or 20 kHz for NMR data collection. A 1 M LiCl aqueous solution was used to set the spectral reference to 0 ppm.

Electrochemical Characterization. Electrochemical measurements were performed on coin cells (model 2032) with lithium metal foils as the reference and counter electrodes at ambient temperature. 70 wt% of as prepared samples, 20 wt% acetylene black (conducting additive), and 10 wt% polyvinylidene fluoride (binder) were blended with N-Methyl-2-pyrrolidone (NMP) to make a slurry and then spread onto a copper foil current collector. After drying at 80 °C for 6 hours, the electrode was punched and then dried under vacuum at 120 °C for 12 hours. The electrodes were then transferred to an argon-filled glove box where both the moisture and oxygen concentrations were kept below 1 ppm. The electrolyte was prepared by dissolving 1 M LiPF\textsubscript{6} in a mixture of ethyl methyl carbonate (EMC), ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1:1 in weight) solution while a Celgard 2325 film was used as the separator. An electrochemical station (CHI660D) was used to obtain cyclic voltammetry (CV) at ambient temperature. CV measurements were performed over a potential range of $5 \times 10^{-3}$–3.0 V (vs. Li\textsuperscript{+}/Li) at a scan rate of $2 \times 10^{-4}$ V s\textsuperscript{−1}. Galvanostatic discharge–charge measurements were performed at different rate on a battery testing system (LAND CT2001A model, Wuhan Jinnuo Electronics Co. Ltd) with a voltage window range from $5 \times 10^{-3}$ to 3.0 V (vs. Li\textsuperscript{+}/Li).

Results and Discussion
The XRD patterns of different molybdenum oxide nanoparticle samples are shown in Fig. 1. All of the XRD peaks for MoO\textsubscript{2} nanoparticles annealed with pure N\textsubscript{2} can be indexed to MoO\textsubscript{2} (Fig. 1a, ICSD:080830), while the sample heated with a high concentration of O\textsubscript{2} (1% O\textsubscript{2} in N\textsubscript{2}) in the flow is completely oxidized to MoO\textsubscript{3} (Fig. 1c, ICSD:080830).
However, MoO$_2$ nanoparticles treated with a smaller fraction of O$_2$ (0.2% O$_2$ in N$_2$) show mixed phases which can be attributed to MoO$_2$, MoO$_3$, as well as a small fraction of Mo$_4$O$_{11}$ (Fig. 1b, ICSD:089340), indicating the nanoparticles have been partially oxidized, noted as MMO. By using the Scherrer equation, the mean diameters of MoO$_2$ and MoO$_3$ nanocrystallites can be determined as 5–8 and 50 nm, respectively, while the average size of MMO is in between.

Figure 2 shows the SEM images of the obtained MoO$_2$, MMO and MoO$_3$ samples. Small agglomerates with a diameter of about 50 nm composed of smaller and round shaped nanoparticles can be observed for the MoO$_2$ sample, while MoO$_3$ are much larger in size (100 to 500 nm). The SEM image of MMO shows this sample is composed of small particles with different sizes, resembling a mixture of the above two materials. The results indicate that MMO are not uniformly oxidized, in agreement with the XRD data.

X-ray photoelectron spectroscopy (XPS) measurement was performed in order to investigate the surface valence states of Mo in MMO, and the results are shown in Fig. 3. The peaks of Mo 3d and O 1s can be observed in the survey spectra (Fig. 3a), and the former was further examined. The two peaks at about 232.0 and 235.0 eV are characteristic of Mo$^{6+}$, and can be attributed to Mo$^{6+}$ (3d$_{5/2}$) and Mo$^{6+}$ (3d$_{3/2}$), respectively. The lower energy peak centered at 229.3 eV can be attributed to Mo$^{4+}$ (3d$_{5/2}$), suggesting that the Mo ions on the surface of MMO are in mixed valence states. The spectrum was fitted into two doublets ascribed to Mo$^{6+}$ (3d$_{5/2}$)/Mo$^{6+}$ (3d$_{3/2}$) and Mo$^{4+}$ (3d$_{5/2}$)/Mo$^{4+}$ (3d$_{3/2}$) (Table 1). The Mo$^{6+}$/Mo$^{4+}$ ratio is determined to be 4.0 according to the line fitting results, hence the valence state of molybdenum on the surface of MMO can be determined as 5.6.

To further investigate the overall valence state of the MMO, TGA-DSC test was carried out to monitor the weight changes as a function of temperature in the air atmosphere and the results are shown in Fig. 4. The small weight loss (about 0.3%) at the temperature lower than 150 °C can be attributed to the loss of absorbed water. The

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Table 1. Results of peak fitting for MMO in the Mo 3d region.

| Peak                  | Position (eV) | Relative Peak Area (%) | FWHM (eV) |
|-----------------------|--------------|------------------------|-----------|
| Mo$^{6+}$ (3d$_{5/2}$) | 229.3        | 12.0                   | 1.0       |
| Mo$^{6+}$ (3d$_{3/2}$) | 232.4        | 8.0                    | 1.0       |
| Mo$^{4+}$ (3d$_{5/2}$) | 232.2        | 48.0                   | 1.9       |
| Mo$^{4+}$ (3d$_{3/2}$) | 235.2        | 32.0                   | 2.0       |
weight increase at 300–500 °C corresponds to the oxidization of MMO (MoOₓ) to MoO₃ in the air and a wide exothermic peak is associated with this process. The total weight increase is 4.30% (Fig. 4), and thus x in MoOₓ can be extracted as 2.63, leading to a calculated average valence state of 5.26 for all Mo ions in the sample MMO. This value determined by TGA is apparently lower than the valence state of surface Mo ions determined by XPS, indicating that the surface of MMO was oxidized to a higher extent compared to the inner part of the material. On the basis of the nominal formula of MoO₂.63 the theoretical capacity of MMO is 1021 mAh·g⁻¹ based on the conversion mechanism.

Cyclic voltammetry (CV) was used to study the Li insertion/extraction behaviors in different samples and the results are presented in Fig. 5a. The redox peaks centered at 1.25/1.53 V and 1.48/1.77 V are attributed to the reversible monoclinic–orthorhombic–monoclinic phase transitions in the partially lithiated LixMoO₂ according to the CV data of MoO₂ nanoparticles (Figure s1a) and previous reports⁶,¹⁹,²¹, consistent with the presence of MoO₂ in MMO which was illustrated in the XRD pattern and the TG curve⁶,²¹. Besides these two redox pairs, there are also intense peaks below 0.5 V, which can be associated with a conversion reaction with lithium, where Mo oxides are reduced completely to metallic

Figure 4. TGA-DSC curve of MMO in air at a heating rate of 5°C/min.

Figure 5. (a) Cyclic voltammograms of MMO at a scan rate of 0.2 mV·s⁻¹ with a mass of 2.5 mg. (b) Discharge and charge curves of MMO at a current of 100 mA·g⁻¹ in the potential window of 3–5 × 10⁻³ V vs. Li⁺/Li. (c) The specific discharge/charge capacity vs cycle number plots for different samples at a current of 200 mA·g⁻¹. (d) Specific capacity vs cycle number curves at different current densities.
Mo along with the formation of Li2O. The curve changes very little in the following cycles, suggesting that the partially lithiated Li1.5MoO2 structure is very stable during the charge-discharge progress, thus MMO is expected to have a good cycling performance25. Meanwhile the difference between the first and following cycles can be attributed to irreversible reactions such as the irreversible phase transition, the decomposition of the electrolyte and the formation of a solid electrolyte interface (SEI) layer22,26.

To further investigate the electrochemical performance of the samples, galvanostatic experiments were performed on the coin cells. Figure 5b shows the charge/discharge plots of MMO at a current of 200 mA·g−1. The initial discharge capacity is 1068.2 mAh·g−1, slightly higher than the theoretical capacity of MMO (1021 mAh·g−1), which can be assigned to some irreversible reactions, e.g. the generation of an SEI layer23,27. In agreement with the CV results, two short discharge plateaus at about 1.55 and 1.26 V can be observed23,21. The expected charge plateaus at around 1.4 and 1.7 V are not clearly visible, which is similar to previously reported MoO2 nanosstructures26. The charge/discharge curves are very stable with continued cycling, suggesting good cycling performances, except that the voltage of discharge plateaus decreases and eventually the plateau can no longer be observed. Since the plateaus are usually attributed to the phase transition in the partially lithiated Li1.5MoO2, the decrease in voltage can be ascribed to the transformation of crystalline phase to amorphous-like structure23,21.

As shown in Fig. 5c, the electrochemical performance of MMO is much better than MoO2 or MoO3. For MoO2, the first discharge capacity is only 670.5 mAh·g−1 while the capacity gradually increases upon cycling and attains 781.7 mAh·g−1 after 15 cycles. This activation process has been reported by other groups and may be attributed to the partial loss of crystallinity of the material during the cycling13,24,29, accompanied with a larger fraction of the material undergoing further conversion reaction instead of stopping at Li2MoO2 phase38. Nonetheless, a rapid capacity deterioration decay can be observed once the capacity reaches the maximum value and remains only a capacity of 325.7 mAh·g−1. Initial capacity of MoO3 is 1017.6 mAh·g−1, however, it drops to 593.4 mAh·g−1 after only 30 cycles due to the big volume changes during cycling. Such decrease can also be observed in MMO, which has a large fraction of MoO2. However, the drop in capacity is much less. The capacity decreases from the first discharge capacity of 1068.2 mAh·g−1 to 842.3 mAh·g−1 after 20 cycles, corresponding to a capacity loss of 12% (calculated based on the capacity of 2nd and 20th cycles). After that, the capacity increases slowly and reaches 976.3 mAh·g−1 after 90 cycles. The discharge capacity of the MMO only decreases slightly to 930.6 mAh·g−1 after 200 cycles, which is equivalent to a capacity retention of 95% of the maximum value of 977 mAh·g−1, demonstrating high capacity and excellent stability. Such high reversible capacity of more than 930.6 mAh·g−1 at 200 mA·g−1 is almost three-fold that of commercial graphite (~330 mAh·g−1). Although the overall profile of MMO’s cycling curve is similar to that of MoO2, the key difference is the capacity decay is much smaller for MMO than MoO2. This decay, which can be seen in many reports of MoO2, is generally assigned to the huge volume and/or structure change during the conversion reaction23,27. Since the volume and structure changes are very limited in the insertion reaction13, the presence of stable partially lithiated Li2MoO2 in MMO is expected to help stabilize the whole electrode and avoid the capacity loss. To further investigate the hypothesis above, the electrochemical performance of the mixed MoO2 and MoO3 sample was prepared by ball milling (MMM) (Figure S2a). Although MMM is also composed of MoO2 and MoO3 with similar proportion (Figure S2a), the electrochemical performance is apparently worse than that of MMO. Although an initial capacity of 1050 mAh·g−1 can be obtained, which is similar to that of MMO, only a capacity of approximately 100 mAh·g−1 can retain after 100 cycles at a current rate of 200 mA·g−1. The very rapid decay can be ascribed to the phase isolation which is expected to accelerate the pulverization process. Owing to the poor electrochemical performances of MoO232, which is the intermediate phase in the transformation from MoO3 to MoO235, the small fraction of Mo4O11, in MMO is also unlikely to be associated with the improved electrochemical properties.

The rate capability of MMO was further investigated and the results are shown in Fig. 5d. The material was tested with the potential range of 5 × 10−3–3.0 V at 0.1 A·g−1, 0.2 A·g−1, 0.5 A·g−1, 1 A·g−1, 2 A·g−1, 5 A·g−1 and 0.1 A·g−1 for 10 cycles each. The specific capacity reaches 994 mAh·g−1 at 0.1 A·g−1, 883 mAh·g−1 at 0.2 A·g−1, 735 mAh·g−1 at 0.5 A·g−1, 644 mAh·g−1 at 1 A·g−1, 538 mAh·g−1 at 2 A·g−1, 397 mAh·g−1 at 5 A·g−1, respectively. A specific capacity of 397 mAh·g−1 at 5 A·g−1 for this material is as high as 40% of its capacity at 0.1 A·g−1 (994 mAh·g−1). The results show that MMO has a better rate capability compared to previous reports26,34. It is noteworthy that this high performance is achieved without coating the active material with carbon based conductors such as graphene.

Table 2 summarizes some recent works on molybdenum oxide based materials as anodes for lithium ion batteries. The specific capacity (930.6 mAh·g−1, 0.2 A·g−1) and cycling performance of MMO in this work excels most of the molybdenum oxide based materials previously reported in the literature, and even those with carbon coating35–41.

To further understand lithium storage mechanisms of MMO, Solid-State NMR and XRD experiments on lithiated samples were performed. 7Li NMR spectroscopy proves to be a powerful method to investigate the relationship between local structures and electrochemical performances of materials for lithium ion batteries and to reveal the electrochemical reaction mechanisms42. 7Li MAS NMR spectra of the MMO and Mo2O3, lithiated to 5 × 10−3 V are given in Fig. 6. A broad resonance can be seen at 2.6 ppm in the spectrum of lithiated Mo2O3, which can be attributed to Li4O which is the product of the conversion reaction. The resonance of the lithiated oxide is broader compared to the spectrum of commercial Li2O standard sample, indicating more complex local structures of the lithium ions after the lithiation process, and/or the magnetic fields generated by the Mo particles22. Similarly, the broad peak at 2.6 ppm in the spectrum of lithiated MMO can be assigned to Li2O formed in the conversion reaction. A sharp peak at −7.0 ppm can also be observed for MMO, indicating that there is another local environment of lithium ions.

The presence of the other lithium compound is further supported by XRD data of lithiated MMO (Fig. 7). The Kapton film was used to protect the air-sensitive fully lithiated sample and its broad background peak can be
### Table 2. Comparison of the capacity of MMO in this work with those of other recently reported molybdenum oxide based materials as anodes for LIBs.

| Materials                                      | Capacity (mAh g\(^{-1}\)) | Current Density (A g\(^{-1}\)) | Cycle number | Year | Ref. |
|------------------------------------------------|-----------------------------|-------------------------------|--------------|------|------|
| a-MoO\(_2\) particles                          | 910                         | 0.1                           | 50           | 2012 | 35   |
| a-MoO\(_x\)-C microballs                       | 733                         | 2                             | 300          | 2013 | 36   |
| F-doped a-MoO\(_x\)                            | 905                         | 0.2                           | 50           | 2014 | 37   |
| MoO\(_3\)/MoO\(_2\) nanonetworks              | 1025                        | 0.2                           | 80           | 2014 | 38   |
| MoO\(_3\)/CNT                                   | 421                         | 0.2                           | 100          | 2014 | 39   |
| MoO\(_2\)/MoO\(_x\) heteronanotubes            | 790                         | 0.2                           | 140          | 2014 | 41   |
| Standing carbon-coated MoO\(_2\) nanosheets ongraphene | 587                         | 1                             | 200          | 2015 | 40   |
| MMO                                            | 930.6                       | 0.2                           | 200          | This Work |

Figure 6. \(^7\)Li solid-state NMR spectra of MMO lithiated to \(5 \times 10^{-3}\) V with a simulation (dashed line in red) fitted with each individual component (solid lines in blue), in comparison to MoO\(_3\) lithiated to \(5 \times 10^{-3}\) V and commercial Li\(_2\)O, for comparison. Spinning rate: 20 kHz.

Figure 7. XRD patterns of MMO and MoO\(_3\) after lithiated to \(5 \times 10^{-3}\) V with the protection of Kapton film, in comparison with the background.
found between 2θ of 10–30°. No distinct peaks can be seen in the pattern of lithiated MoO3, suggesting the poor crystallinity of the product after lithiation. However, pronounced peaks due to Li0.98MoO2, which was previously reported as the product of the insertion reaction of MoO2, appear in the pattern of lithiated MMO. In combination with the results of 7Li MAS NMR spectra of MMO after lithiation, it is clear that two mechanisms including both conversion and insertion reactions are involved in the lithiation of MMO (MoOx) while only conversion reaction is associated with MoO3. Assuming MoO3 in MMO only undergoes a conversion reaction while MoO2 is associated with both insertion/extraction and conversion reaction, the fraction of MoO2 (x) which underwent insertion/extraction reaction in MMO can be estimated in the following equation (considering the theoretical capacity of MoO2 with insertion/extraction mechanism is 210 mAh/g):

\[
C_{\text{MoO}_2} (210 \text{ mAh/g}) \times x + C_{\text{MoO}_3} (838 \text{ mAh/g}) \times (0.37 - x) + C_{\text{LiO}_2} (1117 \text{ mAh/g}) \times 0.63 = 977 \text{ mAh/g}
\]

(the charge capacity of the 1st cycle)

Thus, the value of x can be determined as 0.058, implying 16% of the MoO2 material underwent the insertion/extraction reaction in the MMO material. The capacity of MMO increased after 50 cycles, indicating that more MoO2 underwent conversion reaction. This activation process, which has been reported many times, can be ascribed to the transformation from insertion reaction to conversion reaction, corresponding to the slowly decreasing of discharge plateaus at about 1.5 V.

Two-dimensional exchange (EXSY) 7Li spectra provides more detailed information on the structure of MMO and additional evidences for its better electrochemical properties. With a short mixing time of 1 μs, only two peaks on the diagonal at (2.6, 2.6) and (−7.0, −7.0) corresponding to Li2O and Li0.98MoO2 can be observed in the 2D EXSY spectrum (Fig. 8a). However, small cross peaks at (2.6, −7.0) and (−7.0, 2.6) can be observed at a much longer mixing time of 100 ms for MMO (Fig. 8b) while no peak is present at the same mixing time for MMM (Figure S3). It suggests that the two species in MMO are close in proximity and this mixing time is long enough for chemical exchange processes to occur in which lithium ions move across the interfaces between the two sites. The conclusion that the insertion and conversion reaction products Li0.98MoO2 and Li2O are close in space implies that MoO2 and MoO3 regions are well mixed at the microscale in MMO, while this is not the situation in the sample MMM. The much lower capacity in MMM is presumably associated with the large volume change of MoO3 (104% volume change) during cycling and the resulting aggregation and/or sluggish kinetics of lithium ion insertion for the MoO3 nanoparticles. Since the MoO2 and MoO3 species are not well mixed at the microscale for MMM, inhomogeneous distribution causes phase isolation during cycling, which will lead to pulverization and rapid capacity decay. It has been demonstrated that superior stability can be achieved for the sample with a closer combination between mixed valence lithium vanadates formed in an in-situ transformation than other common coating methods. The boost of the electrical performances may be explained as the results of synergistic interactions. Since transformation from MoO2 to Li0.98MoO2 in insertion reaction only involves small volume/structure change in the very initial cycles, the well dispersed MoO2 helps to keep the integrity of the electrode and prevent the loss of active materials.

Although it is common that only insertion reaction occurs for bulk MoO2, nanostructured MoO2 often undergoes conversion reaction in further lithiation, presumably due to faster kinetics. According to the XRD and NMR results of lithiation samples of MoO2 (Figure S4), the intermediate phase Li0.98MoO2 still exist after 5 cycles, which helps stabilize the structure. The much more stable Li0.98MoO2 in the lithiated MMO nanoparticles may be attributed to the high concentration of MoO2 around MoO2 in MMO. MoO2 is associated with a higher equilibrium potential and a lower activation barrier compared to MoO2, thus conversion reaction will be easier to
occuring during lithiation. The generated amorphous Mo and Li2O have poor electronic conductivity and ionic conductivity, therefore slowing down the kinetics and making further lithiation of Li0.98MoO2 more difficult.

Conclusion
In conclusion, MMO is developed from the moderately oxidation reaction of molybdenum dioxide nanoparticles. The nominal composition of the material can be calculated as MoO2.63, according to the TGA results. MMO shows a high cyclability of 930.6 mAh·g−1 after 200 cycles at a current of 0.200 mA·g−1 as the anode material for lithium ion batteries. The formation of stable Li0.98MoO2 in the lithiation of MMO is confirmed with NMR and XRD on lithiated sample. 2D NMR results confirm that MoO2 and MoO3 are well mixed at the microscale. Both insertion/extraction and conversion reaction mechanisms are involved and the fraction of MoO3, which undergoes the former reactions is estimated to be 16%. The insertion/extraction process stabilizes the electrode material and decrease the volume change generated from conversion reaction of MoO3. This synergistic interaction is believed to be the key to the excellent electrochemical performances and this approach can be applied in many other transition metal oxides to provide advanced electrode materials.

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**Author Contributions**

L.P., W.D. and M.J. contributed to the conception and design of the experiment, analysis of the data and writing the manuscript. D.W. and R.S. carried out design, synthesis and characterization of the materials. D.W. carried out the measurement of solid state NMR and corresponding writing. R.Y. and W.J. carried out the measurement of electrochemical performance. All the authors contributed to discussion on the results and preparation of manuscript. All authors have given approval to the final version of the manuscript.

**Additional Information**

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