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PAPER

Carbon nanotubes-bridged molybdenum trioxide nanosheets as high performance anode for lithium ion batteries

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Abstract

The search for novel nanomaterials driving the development of high-performance electrodes in lithium ion batteries (LIBs) is at the cutting edge of research in the field of energy storage. Here, we report on the synthesis of single wall carbon nanotube (SWNT)-bridged molybdenum trioxide (MoO₃) nanosheets as anode material for LIBs. We exploit liquid phase exfoliation of layered MoO₃ crystallites to produce multilayer MoO₃ nanosheets dispersed in isopropanol, which are then mixed with solution processed SWNTs in the same solvent. The addition of SWNTs to the MoO₃ nanosheets provides the conductive framework for electron transport, as well as a bridge structure, which buffers the volume expansion upon lithiation/de-lithiation. We demonstrate that the hybrid SWNT-bridged MoO₃ structure is beneficial for both the mechanical stability and the electrochemical characteristics of the anodes leading to a specific capacity of 865 mAh g⁻¹ at 100 mA g⁻¹ after 100 cycles, with a columbic efficiency approaching 100% and a capacity fading of 0.02% per cycle. The low-cost, non-toxic, binder-free hybrid MoO₃/SWNT here developed represents a step forward for the applicability of exfoliated MoO₃ in LIB anodes, delivering high energy and power densities as well as long lifetime.

1. Introduction

The worldwide lithium-ion batteries (LIBs) market is increasing with a relevant growth rate of more than 20% per year [1], with an estimated global market reaching \$130 billion in 2025 [2]. Today, LIBs find the main application in portable electronic devices [3], while the increasing demand in the transport sector, i.e. full electric vehicles (EVs) and hybrid electric vehicles (HEVs) [4], will drive the growth of LIBs market towards automotive and industrial applications [1]. Moreover, energy storage for grid balancing and micro-grids, e.g. residential storage battery in conjunction with photovoltaic systems, will also play a role for the growth of LIBs market [5]. Current LIBs [6], based on the capture and release of lithium ions, are usually composed by an intercalated lithium compound cathode (e.g. LiCoO₂ or LiFePO₄), a graphitic-based anode and an electrolyte [6, 7], yielding a theoretical specific energy density of 387

Wh kg⁻¹ (with LiCoO₂ as cathode) [7] and a measured energy density of 120–150 Wh kg⁻¹ [7].

Crucial to the performance of these rechargeable batteries is the specific capacity (or gravimetric capacity, i.e. total ampere-hours -Ah- available when the battery is discharged at a certain current density, per unit weight) to evaluate the capability of lithium ions storage in the active materials [4]. In this regard, LIBs are still limited by the specific capacity of the commercial active materials, e.g. graphite anode with a theoretical specific capacity of 372 mAh g⁻¹ [8]. For this reason, a current research effort focuses on the exploitation of alternative anodic materials with high theoretical specific capacity such as Si (3579 mAh g⁻¹) [9], Sn (994 mAh g⁻¹) [10], and SnO₂ (782 mAh g⁻¹) [11]. However, the full development of such high-performance anode materials has been hindered by the significant capacity fading owing to the large volume contraction/expansion (100–300% with respect to the initial volume) [12] during charge–discharge cycling [13].

Another promising strategy that is emerging in the last few years is to replace graphite with other layered anode materials, i.e. transition metal oxides [14–18] and graphene-based materials [19–30], which are expected to improve the energy storage of LIBs. In this context, graphene and its derivatives, i.e. reduced graphene oxide (RGO) [19, 20] and graphene nanoplatelets (GNPs) [21], have been already largely explored for the realization of LIB anodes [22]. The aforementioned graphene-based materials display larger theoretical specific capacity (i.e. 744 mAh g^{-1} assuming lithium adsorbed on both sides of graphene to form Li_2C_6) [23] when compared to graphite, electrochemical and thermal stability within the LIBs operational temperature range ($-20/60^\circ\text{C}$) [24], offering additional properties of flexibility and/or stretchability [25]. However, they also suffer severe limitations. In fact, in single-layer graphene (SLG), Li storage is not thermodynamically favoured, with low value of Li uptake [26–28]. So an hypothetical SLG anode will not be an efficient solution. Moreover, the morphology (i.e. lateral size and thickness) of the flakes strongly influences the Li^+ storage capability of few- (FLG) and multi-layer graphene (MLG) flakes [29]. Indeed more capacity is delivered at high potentials upon flake size reduction, resulting in reduced and non-constant voltage output from the battery, a detrimental factor on the voltage efficiency [24]. Finally, RGO and GNPs experience critical issues for LIB applications. In fact, RGO show large irreversible capacity [19, 20] and voltage hysteresis between lithiation and de-lithiation [30], while GNPs have not yet demonstrated considerable gain in maximum specific capacity with respect to graphite [21, 25].

Metal oxides are another class of layered materials that can be used as anode materials in LIBs [31, 32]. Amongst them, MoO_3 , which has already shown promise for various applications, including optical devices [33], catalysts [34], sensors [35] and field emission devices [36, 37], is a promising candidate for electrochemical storage applications [38–44]. In particular, the intrinsic structural anisotropy of α - MoO_3 , i.e. the thermodynamically stable orthorhombic phase [45, 46], offers the possibility of reversible electrochemical insertion of lithium [47]. In LIB applications, α - MoO_3 has been firstly proposed as a cathode material [48, 49], but its low voltage plateaus ($3.2\text{--}2.0 \text{ V}$ versus Li^+/Li) [14, 50] has hindered its practical exploitation [51–54]. Contrariwise, α - MoO_3 has been demonstrated a very promising anode material thanks to its high theoretical specific capacity of 1117 mAh g^{-1} [55, 56]. Additionally, the interlayer spacing as large as 0.69 nm of α - MoO_3 [57, 58], compared to 0.34 nm of graphite, guarantees its Li host capability [59]. Moreover, its higher intercalation voltages ($1.5\text{--}2.3 \text{ V}$ versus Li^+/Li), with respect to that of graphite ($<0.4 \text{ V}$ versus Li^+/Li), could reduce the safety problems caused by the decomposition of electrolyte, especially for the utilization in HEVs [60].

The electrochemical performances of bulk MoO_3 are limited by its own poor ionic [61] and electrical (i.e. $\sim 10^{-5} \text{ S m}^{-1}$) [62] conductivity, as well as volume expansion during charge–discharge processes [47, 60, 63, 64]. To overcome the aforementioned problems, one of the most encouraging strategies is to reduce the lateral size of bulk MoO_3 by nanostructuring [47, 60–68], and mix the resulting MoO_3 nanostructures with carbon-based nanomaterials, such as amorphous carbon [44], carbon nanotubes (CNTs) [63] and graphene [69], to form hybrid materials. The exploitation of these various nanostructured MoO_3 hybrids as anode materials have demonstrated significant improvement, with respect to the bulk MoO_3 , in term of specific capacity [69, 70] and electrochemical stability [47, 60, 63, 64]. Nevertheless, the costly production processes used [47, 60–64, 68], e.g. chemical vapor deposition (CVD) [56] or hydrothermal methods [47, 61, 64, 71], pose scalability challenges towards practical industrial application [56, 57]. Additionally, the use of toxic materials [72, 73] as well as binders [74, 75] are also limiting factors for practical use.

Recently, liquid phase exfoliation (LPE) [76, 77] has attracted increasing attention to obtain nanoscale graphene and other 2D layered materials, which have strong covalent intra-layer bonding [78], but weak out-of-plane inter-layer interactions [79–81]. Henceforth, it is possible to peel off individual layers from the parent bulk crystal by supplying sufficient energy [82]. Thus, this process has become a widely used method for the production of a range of 2D flakes [74] (e.g. MoO_3) [83] from their parent bulk crystals [84]. During the LPE process, the inter-sheet forces are broken by the input of either shear or ultrasonic energy in the presence of a stabilizing liquid [73, 85]. The resultant exfoliated flakes are generally defect-free and unfunctionalized [86, 87].

In this paper, we demonstrate that multi-layer MoO_3 nanosheets produced by LPE of layered MoO_3 crystallites combined with single wall carbon nanotubes (SWNTs) can be used as an active binder-free material for LIBs. The hybrid anodes are produced by mixing multilayer MoO_3 nanosheets with solution processed SWNTs. Both the MoO_3 exfoliation process and the SWNTs de-bundling are carried out in isopropanol, allowing a simple deposition onto the copper substrate. The designed binder-free solution processed hybrid MoO_3 /SWNT anode displays a specific capacity of 865 mAh g^{-1} at 100 mA g^{-1} after 100 cycles, with a columbic efficiency of 99.7%. The SWNTs addition determines a network structure with the MoO_3 providing (1) long channels for electronic charge transport; (2) an active anode material, instead of polymeric binder, offering extra capacity for Li ions storage; (3) a buffer frame in the electrode, which reduce the capacity fading caused by the volume expansion of MoO_3 flakes during the lithiation process. To further confirm the essential roles of SWNTs, we also tested multilayers MoO_3 combined with carbon black (CB) nanoparti-

cles, which are not able to create the network structure seen with SWNTs, yielding a significant capacity fading of the resulting battery. These results set the basis for the exploitation of exfoliated 2D MoO₃ sheets as anodic materials in Li-ion batteries.

2. Experimental

2.1. Preparation of MoO₃ flakes and MoO₃/SWNT hybrid structure

2.1.1. Materials

MoO₃ powder is purchased from Sigma Aldrich (99.98%, CAS 1313-27-5) and SWNTs are purchased from Carbon Solutions inc. All materials are used without any further purification.

2.1.2. LPE MoO₃ nanosheets preparation

Molybdenum trioxide powder (240 mg) is added to 2-propanol (IPA) (80 ml) in a 100 ml open top, flat bottomed beaker. The dispersion is ultrasonicated using a horn probe sonic tip (VibraCell CVX, 750 W, 25% amplitude) for 5 h. The sonic tip is pulsed for 6 s on and 2 s off to avoid damage to the processor and reduce any solvent heating. To minimize heating effects, an external cooling system circulated cooled water (5 °C) around the beaker during ultrasonication. To remove any un-exfoliated material the ultrasonicated dispersion is filled in glass vials (~30 ml) and ultracentrifuged at 1 krpm (~100 g) for 30 min. The supernatant is decanted (~20 ml) and further ultracentrifuged at 5 krpm for 105 min to remove small flakes. The supernatant is decanted (containing small flakes) and discarded while the sediment is re-dispersed in fresh IPA.

2.1.3. SWNTs dispersion preparation

P3 SWNTs are dispersed in IPA at a concentration of 0.1 g l⁻¹ and ultra sonicated in both a horn sonic probe and a sonic bath to achieve a completely homogeneous dispersion. The procedure involves horn probe ultrasonication (30 min) followed by 1 h in a sonic bath and an additional 30 min in the horn probe tip.

2.1.4. CB dispersion preparation

Carbon black is dispersed in IPA at a known concentration (0.25 g l⁻¹) and bath ultrasonicated for 2 h.

2.1.5. MoO₃/SWNT/CB hybrid

The as produced MoO₃, SWNTs and CB dispersions are then mixed, without centrifugation, to form hybrid structures of known wt%. Accurate weighing of an alumina membrane (pore size 25 nm) before and after filtration of MoO₃ dispersion allowed determining the concentration.

2.2. Characterization of SWNTs, CB, MoO₃ flakes and MoO₃/SWNT hybrid structure

Transmission electron microscopy (TEM) images of MoO₃, SWNT, CB and MoO₃/SWNT hybrid are taken with a JOEL JEM 1011 transmission electron microscope, operated at 100 kV. The samples are then diluted 1:10 with pure IPA associated with 10 min ultra-sonication. 100 µl of the resulting dispersions are drop-cast at room temperature onto carbon coated copper TEM grids (300 mesh), and subsequently dried under vacuum overnight. Raman measurements are carried out with a Renishaw 1000 using a 50× objective, a laser with a wavelength of 532 nm and an incident power of ~1 mW. The samples are drop-cast onto a Si wafer (LDB Technologies Ltd), with 300 nm thermally grown SiO₂.

2.3. Fabrication and characterization of MoO₃ and MoO₃/SWNT electrodes

50 mg of MoO₃ nanosheet and MoO₃/SWNT hybrid samples are dried and re-dispersed in 5 ml ethanol via ultra-sonication for 15 min. Subsequently, the aforementioned samples are drop-cast on the Cu foils as supporting substrates in a circular shape with a diameter of 15 mm at 40 °C in air. Then, the as deposited films are dried at 120 °C and 10⁻³ bar pressure for 12 h in oven (BÜCHI, B-585). The mass loading of the active materials are calculated by subtracting the average weight (obtained with balance of Mettler Toledo XSE104) of bare Cu foil with the same area, from the total weight of the electrodes. Scanning electron microscopy (SEM) images of the MoO₃, MoO₃/CB and MoO₃/SWNT films are taken by a field-emission scanning electron microscope FE-SEM (Jeol JSM-7500 FA), without any conductive coating. Raman measurements of the as-prepared MoO₃, SWNT, CB and MoO₃/SWNT films are carried out in the same experimental conditions reported for the characterization of the dispersions, see section 2.2.

2.4. Assembling and electrochemical tests of MoO₃ based anode

MoO₃ and MoO₃/SWNT based half-cell assembling. The MoO₃, MoO₃/CB and MoO₃/SWNT based anodes are performed in half-cells configuration against Li foils (Sigma-Aldrich) as the counter electrodes. Half cells are assembled in coin cell (2032, MTI) in an argon filled glove box (O₂ and H₂O < 0.1 ppm) at 25 °C, using 1M LiPF₆ in a mixed solvent of ethylene carbonate/dimethylcarbonate (EC/DMC, 1:1 volume ratio) as electrolyte (LP30, BASF), as well as glass-fiber as separator (Whatman GF/D).

Electrochemical tests. The cyclic voltammetries (CVs) are performed at a scan rate of 50 µV s⁻¹ between 1 V and 5 mV versus Li⁺/Li with a Biologic,

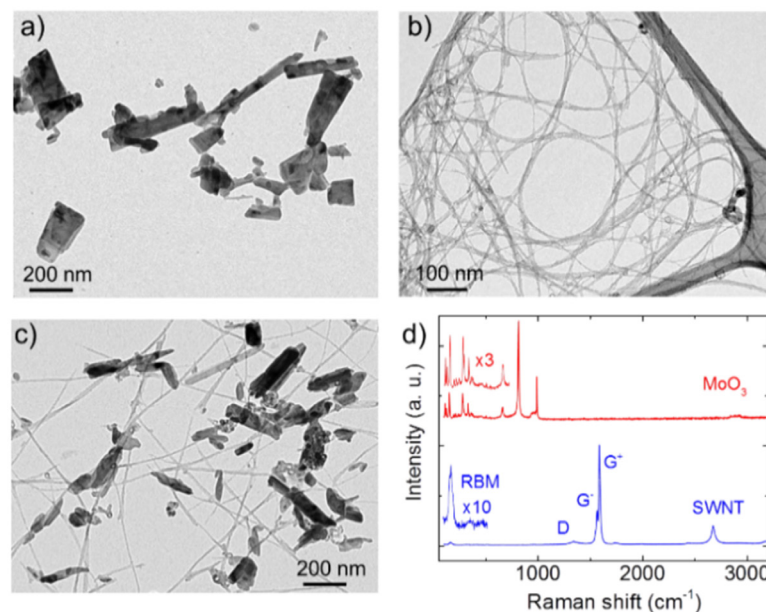


Figure 1. Bright-field TEM images of (a) MoO₃ flakes, (b) SWNTs and (c) MoO₃/SWNT hybrid dispersed in IPA. (d) Raman spectra of MoO₃ (in red) and SWNTs (in blue) taken at an excitation wavelength of 514.5 nm.

MPG2 potentiostat/galvanostat. The electrochemical impedance spectroscopies are collected with a VMP3 (BioLogic). All the electrochemical measurements are performed at room temperature. Constant current charge/discharge galvanostatic cycles are performed for the as prepared binder-free anodes in half-cell and in full battery configuration at a different current density, using a battery analyzer (MTI, BST8-WA). The charge/discharge cycles are performed at different rates at room temperature.

3. Results and discussion

3.1. Properties of MoO₃, MoO₃/CB and MoO₃/SWNT dispersions

The synthesis of the MoO₃/SWNT hybrid anode for LIBs starts with the solution processing of the two nanomaterials. The MoO₃ flakes in dispersions are obtained by LPE of pristine MoO₃, while the SWNTs are prepared in IPA by tip ultrasonication, see Experimental for detailed information about their preparation, as well as for the processing of the CB nanoparticles.

The morphology of the as-produced MoO₃ and SWNTs are analysed by TEM. Figure 1(a) shows MoO₃ flakes with lateral sizes ranging from 50 to 300 nm, while figure 1(b) shows that the SWNTs are in bundles of ~10 nm in diameter, forming a spider web-like network onto the TEM grid. The TEM image of the hybrid MoO₃/SWNTs sample (see figure 1(c)), clearly shows the bundles of SWNTs acting as bridges to connect isolated MoO₃ flakes, forming an interconnected network in the hybrid MoO₃/SWNTs. The TEM of CB, reported in the supplementary information -S.I.- (see

figure S3(b) (stacks.iop.org/TDM/5/015024/mmedia)), shows a particle size distribution of ~50 nm. We further carried out the characterization of the morphological properties of the dispersed materials by Raman spectroscopy, which is a fast and non-destructive technique commonly used to identify type of defects, doping, disorder and chemical modifications of nanomaterials [88]. In figure 1(d) we show the Raman spectra of MoO₃, in blue, and SWNTs, in red. The full spectroscopy characterization, i.e. optical absorption and Raman, of the as-prepared MoO₃, SWNTs and CB nanoparticles are discussed in the S.I.

The as-prepared samples are then exploited for the realization of electrodes, i.e. anodes, for LIBs. In particular, solution processed MoO₃ flakes and the MoO₃/SWNT hybrid (9:1 ratio) is deposited onto Cu substrates. A reference sample, i.e. MoO₃ mixed with 10% CB, is also prepared by using the same process. The mass loading of MoO₃, MoO₃/SWNT and MoO₃/CB in the corresponding electrodes has been calculated as 0.80 mg, 0.74 mg and 0.75 mg, respectively. The morphology of the MoO₃/SWNT and MoO₃/CB electrodes is characterized by SEM. The SEM image of the MoO₃ electrode (figure 2(a)) shows MoO₃ flakes with regular polygonal shapes, which are homogeneously distributed onto the Cu substrate.

Figure 2(b) shows how the morphology of the hybrid MoO₃/SWNT is dominated by the MoO₃ flakes inserted in the mesoporous network of SWNT bundles. In contrast, the morphology of the MoO₃/CB electrode is dominated by large aggregates of CB, ~400 nm in diameter, with a few MoO₃ flakes observed in figure 2(c).

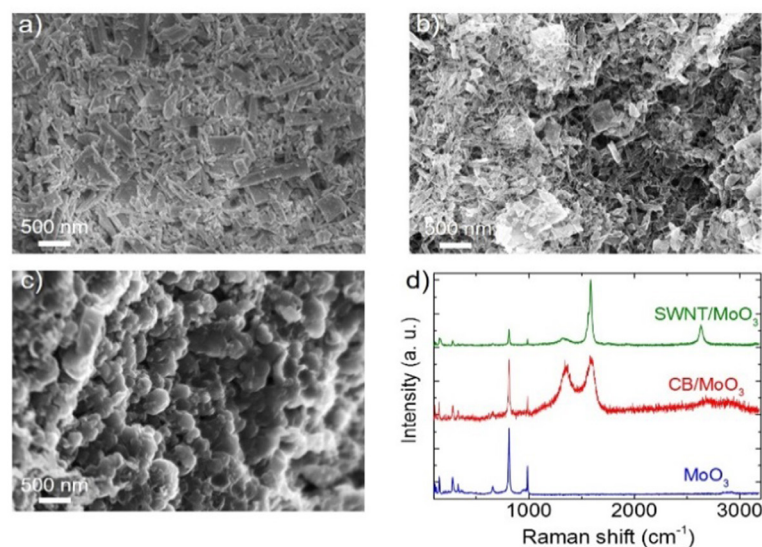


Figure 2. Scanning electron microscope images of (a) MoO₃, (b) MoO₃/SWNT and (c) MoO₃/CB deposited onto copper substrates. (d) Raman spectra of the MoO₃/SWNT (green), MoO₃/CB (red) and MoO₃ (blue) electrodes, deposited onto copper substrates.

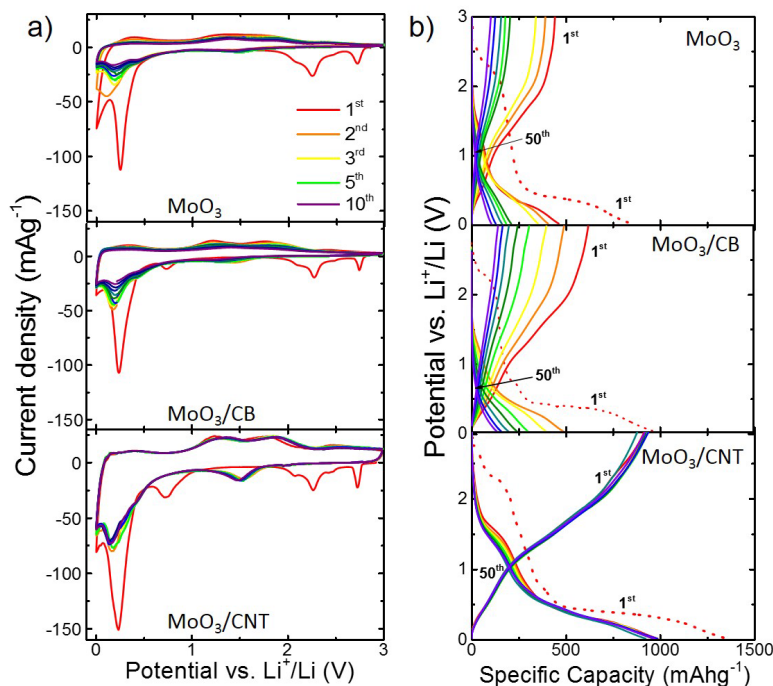


Figure 3. (a) Cyclic voltammograms and (b) charge/discharge voltage profiles of MoO₃, MoO₃/CB and MoO₃/SWNT as anodes against Li foil in half cell configuration.

3.2. Electrochemical properties of MoO₃, MoO₃/CB and MoO₃/SWNT electrodes

In order to fully understand the optimal SWNTs/MoO₃ weight ratio on the electrochemical performances of the MoO₃/SWNT hybrid anodes, we prepared other two samples with different SWNTs/MoO₃ weight ratio of 2:8 and 3:7, respectively, see Experimental. The Raman and SEM characterization of the electrodes are presented and in depth discussed in the S.I. As shown in figure S4, the three MoO₃/SWNT hybrid anodes show a homogenous coverage of SWNTs and MoO₃ nanoflakes onto the Cu substrates.

The CVs (figure 3(a)) of the three samples, i.e. MoO₃, MoO₃/CB and MoO₃/SWNT are collected at a scan rate of 50 $\mu\text{V s}^{-1}$ starting from 5 mV versus Li⁺/Li potential, to cover the lithiation processes in both MoO₃ and SWNT [89]. In the first reduction sweep, the MoO₃ exhibits two peaks at 2.3 and 2.7 V, which can be linked with the insertion of Li ions into the interlayers of the MoO₃ structure to form Li_xMoO₃, and another peak at 0.4 V, which corresponds to the conversion reaction of Li_xMoO₃ into Mo and Li₂O [42, 54, 93].

The two processes determine, the accommodation of six Li ions in each MoO₃, reaching theoretical

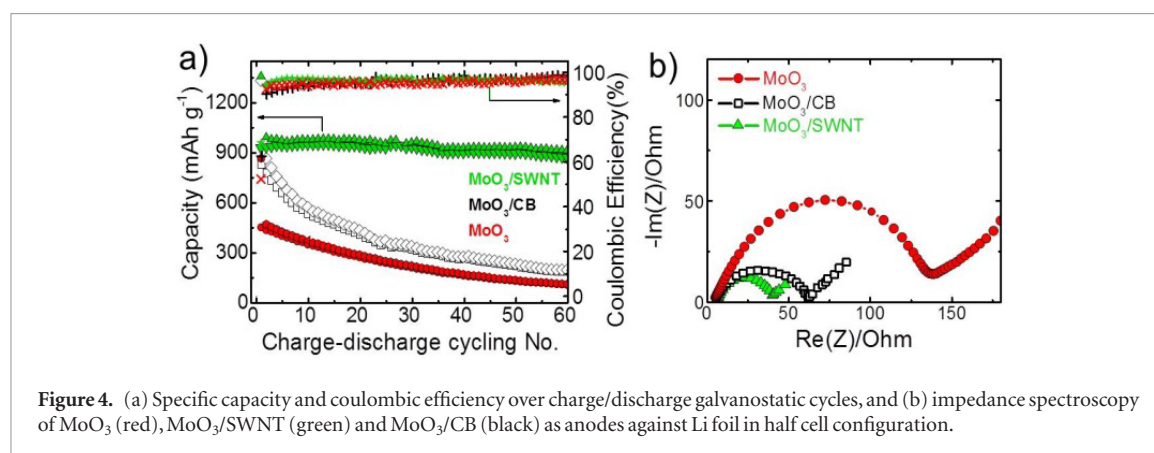
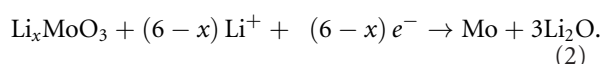
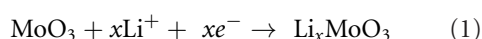


Figure 4. (a) Specific capacity and coulombic efficiency over charge/discharge galvanostatic cycles, and (b) impedance spectroscopy of MoO₃ (red), MoO₃/SWNT (green) and MoO₃/CB (black) as anodes against Li foil in half cell configuration.

specific capacity of 1117 mAh g⁻¹ [56, 57], as summarized by equations (1) and (2) [54, 93],



In the reverse oxidation process, metallic molybdenum is converted into amorphous MoO₂, in the 1.0 V–2.2 V range [90]. From the 2nd cycle onward, a clear shift is observed in the conversion reaction peak at 0.4 V, which is consistent with the formation, upon oxidation, of MoO₂ with lower reactivity with respect to MoO₃ [97]. Furthermore, in the second cycle a new peak, at 1.5 V, appears which can be assigned to the lithium insertion into amorphous MoO₂ [91, 97]. For the MoO₃ and the hybrid MoO₃/CB samples, the reduction peaks at 1.5 V and 0.4 V rapidly disappear during the following 8 cycles. On the contrary, in the case of MoO₃/SWNT sample the intensity of these two peaks is maintained from cycle 2 to cycle 10, leading to a remarkable improvement on its electrochemical stability with respect to the other two samples.

Figure 3(b) shows the charge–discharge voltage profiles of bulk MoO₃ at 100 mA g⁻¹, in order to get a complete electrochemical response for the Li ion transfer [92], during the lithiation/de-lithiation process at the anode. In the 1st charge (lithiation) process, two plateaus at 2.3 V and 0.4 V are observed in all the three samples. These two plateaus have already been attributed to the formation of Li_xMoO₃ and its following conversion reaction into metallic Mo and LiO₂, respectively [42, 54, 93]. These reactions have also contribution on the large initial specific capacity obtained in the three samples, i.e. 864 mAh g⁻¹ for MoO₃, 1332 mAh g⁻¹ for MoO₃/CB, and 1357 mAh g⁻¹ for MoO₃/SWNT. The higher initial specific capacity shown by both the MoO₃/SWNT and MoO₃/CB samples, compared with the MoO₃ sample, can be associated to the enhanced electrical conductivity in the hybrid electrodes due to the presence of the carbon nanomaterials [65, 93]. On the contrary, significant differences of the three samples are shown by the specific capacities obtained at the 1st discharge (de-lithiation) process. In fact, initial specific capacities of 481, 625 and 962 mAh g⁻¹ are achieved for the

MoO₃, MoO₃/CB, and MoO₃/SWNT samples, respectively. For all the 3 samples, the capacity drop between the 1st charge and discharge processes (see figure 4(a)), is caused by the combination of several irreversible processes, including: (1) the solid electrolyte interphase (SEI) formation [62]; (2) the structural modulation during Li⁺ insertion/extraction into the inter-layers and intra-layers of MoO₃ [94]; (3) the conductivity loss caused by the electrode pulverization upon lithiation/de-lithiation [95].

For the MoO₃ and MoO₃/CB samples, we observed a coulombic efficiency (the ratio between discharge and charge capacities) at the 1st cycle as low as 55.7% and 46.9%, respectively, see figure 4(a). Moreover, both samples show capacity fading upon cycling, which is the main drawback of MoO₃ anodes due to the pulverization of the electrode [65], with capacity loss of 84% and 64%, respectively, after 60 cycles. Alternatively, the MoO₃/SWNT sample shows a coulombic efficiency as high as 70.9% at the 1st cycle, a value which is significantly enhanced compared to the MoO₃ and MoO₃/CB samples. Additionally, the MoO₃/SWNT sample shows a tangible improvement on the stability of the electrochemical performance, delivering reversible capacity of 950 mAh g⁻¹ at 50th cycle, with only a 1.2% capacity loss from the 1st cycle.

In order to further understand the different electrochemical performance of the three MoO₃-based electrodes, we carried out electrochemistry impedance spectroscopy (EIS) for all the three samples at charged state, after 60 cycles. The Nyquist plots of the electrodes are presenting a semi-circle at high-to-medium frequency [60], demonstrating the different interface resistances in the three samples. The interface resistance occurring at high frequency is associated with phenomena such as Li⁺ ion diffusion through the SEI film and/or in the active material, and the contact layer between the electrode and current collector [96–98].

As obtained from figure 4(b), the interface resistance of the MoO₃ sample is ~160 Ω, which is significantly reduced to ~80 Ω for the MoO₃/CB sample. The MoO₃/SWNT hybrid structure gives the lowest value of interface resistance, i.e. ~40 Ω, which is one fourth and one half with respect to the ones shown by the MoO₃ and MoO₃/CB-based electrodes,

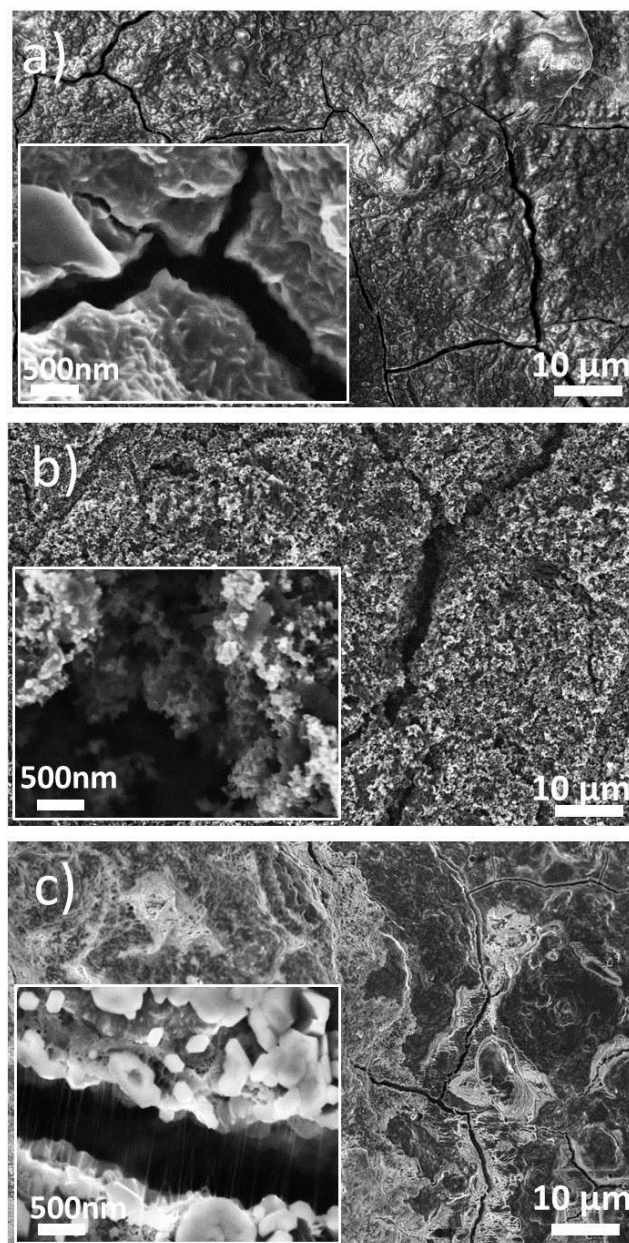


Figure 5. SEM images of (a) MoO_3 , (b) MoO_3/CB and (c) MoO_3/SWNT electrodes after 60 charge/discharge galvanostatic cycles.

respectively. The reduction of the interface resistance upon the addition of carbon additives, especially SWNTs, compared with the MoO_3 , might be attributed to the different structural morphology of the electrodes after lithiation/de-lithiation processes [60, 61].

Thus, in order to understand the relation between the electrochemistry performance of the three samples and their structural morphology after charge-discharge cycles, we carried out post-mortem SEM measurements on MoO_3 , MoO_3/CB and MoO_3/SWNT electrodes after 60 charge/discharge cycles. As shown in figure 5(a), the MoO_3 electrode clearly presents cracks and fractures with width of 200–400 nm, likely caused by the volume change during the charge/discharge cycles. These cracks determine a drop in the electrical conductivity, with consequent capacity fading [99, 100], as clearly presented in figure 4. As shown

in figure 5(b), large cracks over $1\ \mu\text{m}$ are observed in the MoO_3/CB electrode as well. Even if, compared to free MoO_3 , the presence of CB seems able to furnish better electrical conductivity during the first cycles MoO_3/CB electrodes still suffer a remarkable capacity fading upon cycling. This is likely due to the inability of CB to keep the anode material in continuous contact with the current collector [102, 103]. Although the MoO_3/SWNT sample shows cracks after 60 cycles, the cracks are much narrower with respect to the ones presented by the MoO_3 and MoO_3/CB electrodes.

Moreover, the carbon network of nanotubes ensures high electrical conductivity upon the expansion/contraction processes of MoO_3 . This conductive framework is therefore beneficial for both mechanical stability [101] and the specific capacity of the anodes.

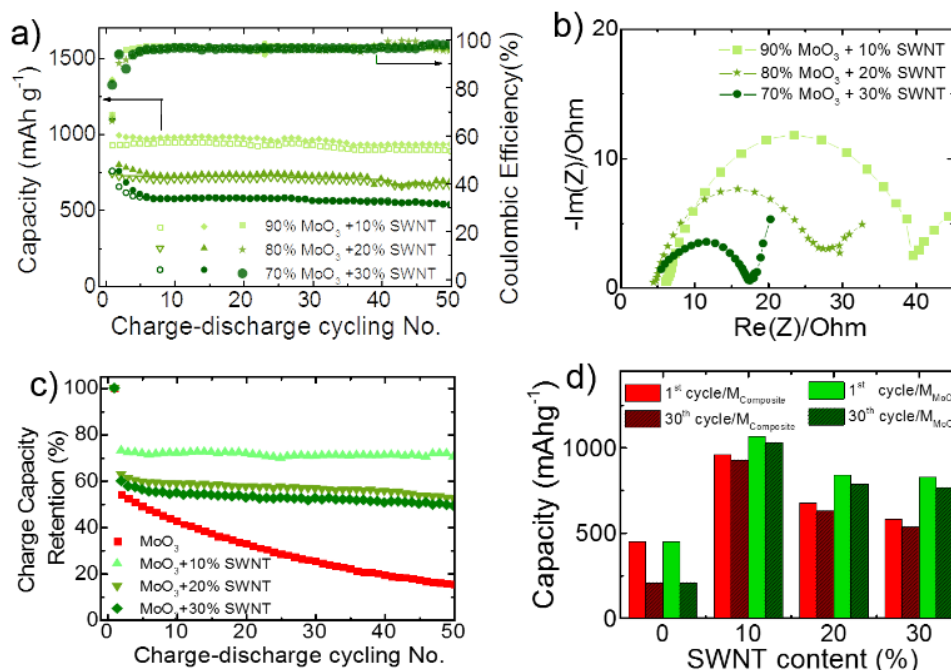


Figure 6. (a) Specific capacity and coulombic efficiency over charge/discharge galvanostatic cycles, and (b) impedance spectroscopy of MoO₃/SWNT hybrid electrodes with different SWNT weight ratios as anodes against Li foil in half cell configuration. (c) Capacity retention of MoO₃/SWNT hybrid anodes and (d) Specific capacity of MoO₃/SWNT hybrid anode calculated with respect the weight of MoO₃ (red) and the hybrid structures, respectively (green).

3.3. Electrochemical properties of MoO₃/SWNT electrodes with different mix ratio

From the obtained results, it is clear that the SWNTs addition (10% with respect to the MoO₃ flakes) is beneficial for the electrochemical properties of the electrodes. Thus, in order to further investigate the contribution of the SWNTs addition in the MoO₃/SWNT hybrid anode, we designed other two electrodes, adding SWNTs to the MoO₃ flakes at a weight ratio of 20% and 30%, with mass loading of 0.74 mg and 0.76 mg, respectively. As shown in figure 6(a), while the percentage of SWNTs in the MoO₃/SWNT electrodes rises from 10% to 30%, the initial capacities of the three samples reach 1357, 1161 and 1044 mAh g⁻¹, with corresponding discharge capacity at the first cycle of 927, 675, and 566 mAh g⁻¹, respectively. The specific capacity and coulombic efficiency (see figure 6(a)) demonstrate that all the hybrid electrodes with different mixed ratios show remarkable stable cyclability up to 50 cycles, if compared with the MoO₃ anode.

The post-mortem SEM images of the three MoO₃/SWNT electrodes shown in figures S5(b)–(d) clearly demonstrate that the SWNTs in the MoO₃/SWNT electrode create a network between the cracked ‘islands’ following the MoO₃ volume change during charge/discharge cycles [65]. Notably, the width of the cracks is reducing with the percentage increase of SWNT in the MoO₃/SWNT hybrids. A possible explanation could be linked with the fact that the increasing amount of SWNTs, as buffer between the MoO₃ flakes, can efficiently attenuate the volume change during

charge/discharge cycles, reducing the mechanical degradation of the electrodes.

The EIS results of the 3 samples shown in figure 6(b), demonstrates how the higher is the percentage of SWNTs in the hybrid MoO₃/SWNT electrodes, the lower is their charge transfer resistance. In fact, a charge transfer resistances of ~40 Ω, ~30 Ω and ~17 Ω have been obtained for the sample with 10%, 20% and 30% of SWNTs with respect to the MoO₃ flakes, respectively. However, although higher percentage of SWNTs (i.e. 20–30%) in the hybrid structure can provide better electrical conductivity (i.e. charge transfer resistances of 30 Ω and 17 Ω for the electrodes containing 20% and 30% of SWNTs with respect to the MoO₃ flakes) this is not directly associated to an increase of the electrode specific capacity. In fact, the increasing percentage of SWNT has determined a tangible decrease of the specific capacity with respect to the total loading of MoO₃/SWNT hybrid electrodes. This could be linked with the high irreversible capacity that affects CNTs-based anode for LIBs [102]. In fact, the irreversible capacity increases from 32% for the 10% MoO₃/SWNTs sample to 46% in the case of 30% MoO₃/SWNTs one. Moreover, the 10% MoO₃/SWNTs sample shows the highest capacity retention (71.6% after 50 cycles) over charge/discharge cycles, obtained by dividing the charge-capacity to the initial capacity (see figure 4(a)), amongst the electrodes, i.e. the hybrids MoO₃/SWNTs and the MoO₃ one.

Moreover, we have also calculated the specific capacity of each electrode, as shown in figure 6(c), labeled by different SWNTs content from 0 to 30%. The

specific capacities are calculated using the mass loading of MoO_3 and MoO_3/SWNT , respectively. In both cases, the 10% SWNT sample reaches the highest specific capacity of $1028 \text{ mAh g}_{\text{MoO}_3}^{-1}$ ($926 \text{ mAh g}_{\text{MoO}_3/\text{SWNT}}^{-1}$), see figure 6(d), which represent the 92% of the theoretical specific capacity of MoO_3 [55, 56]. As summarized in table S1 (see S.I.), the performance of our MoO_3/SWNT binder-free anode favorably compare with state of the art MoO_3 -based LIBs [39, 42, 44, 49, 56, 60, 65, 72, 103, 104]. The reported electrochemical analysis indicates that the addition of 10% SWNT in the hybrid structure with MoO_3 flakes represents the best compromise in term of mechanical and electrochemical properties of the as-produced anodes.

4. Conclusion

By exploiting the combination of multilayer MoO_3 nanosheets, produced by LPE of layered MoO_3 crystallites, with solution processed SWNTs we demonstrated a high performance binder-free $\text{MoO}_3/\text{SWNTs}$ hybrid anode for LIBs. Contrary to CB nanoparticles, the SWNTs addition determines a network structure with the MoO_3 , which is beneficial for the mechanical and (electro)chemical performances of the as-produced anode by providing (1) long channels for electronic charge transport; (2) an active anode material, instead of polymeric binder, offering extra capacity for Li ions storage; (3) a buffer frame in the electrode, which reduce the capacity fading caused by the volume expansion of MoO_3 flakes during the lithiation process. The designed binder-free solution processed hybrid MoO_3/SWNT (90:10) anode has demonstrated a specific capacity of 865 mAh g^{-1} at 100 mA g^{-1} after 100 cycles, with a columbic efficiency of 99.7% and a capacity fading of 0.02% per cycle. We believe that the low-cost, non-toxic, binder-free hybrid MoO_3/SWNT can boost the development of high-performance anodes for LIBs.

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