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Blend formed by oxygen deficient $MoO_{3-\delta}$ oxides as lithium-insertion compounds

A.M. Hashem^{1,2}, S.M. Abbas³, A.E. Abdel-Ghany¹, A.E. Eid¹, A.A. Abdel-Khalek³, S. Indris², H. Ehrenberg², A. Mauger⁴, C.M. Julien⁵

¹National Research Centre, Inorganic Chemistry Department, 33 El Bohouth St., (former El Tahrir St.), Dokki-Giza 12622, Egypt

²Karlsruhe Institute of Technology (KIT), Institute for Applied Materials –Energy Storage Systems (IAM- ESS), Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany

³Department of Chemistry, Faculty of Science, Beni-Suef University, Beni-Suef 62111,

Egypt

⁴Sorbonne Universités, Univ. UPMC, Paris-6, PHENIX, UMR 8234, 4 place Jussieu, 75005 Paris, France

⁵Sorbonne Universités, Univ. UPMC, Paris-6, IMPMC, 4 place Jussieu, 75005 Paris, France

Corresponding author: <u>christian.julien@upmc.fr</u> (C.M. Julien)

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Abstract

Oxygen deficient Mo_xO_y 200 nm-thick particles were synthesized by a citrate sol-gel method using ammonium heptamolybdate tetrahydrate as a source of Mo and heat treated with a small fraction of zirconia under reducing atmosphere. The samples were investigated by Xray powder diffraction (XRD), thermal gravimetric analysis (TGA), scanning electron microscope (SEM) and Raman spectroscopy (RS). The structural analyses show that the composite is a blend formed by layered α -MoO₃, orthorhombic oxygen deficient phases MoO_{3-δ} with δ =0.25 (γ -Mo₄O₁₁) and α -ZrMo₂O₈. The insertion of lithium into the lattice was performed by electrochemical method. Redox peaks were observed for the MoO_{3-δ} composite attributed to distinct Li⁺-ion insertion/extraction reactions in the MoO₃ and Mo₄O₁₁ hosts. The cyclic performance revealed improved reversibility, rate capability, and electrochemical stability of the ZrMo₂O₈-decorated composite with respect to the bare molybdenum oxides. At C/10 rate, the composite delivered a stable reversible capacity of 135 mAh g⁻¹ after the 50th cycle. At a rate of 2C the reversible capacity is maintained at 118 mAh g⁻¹, approximately twice the capacity observed for the MoO₃ particles alone.

1. Introduction

MoO₃ is currently investigated for many purposes. Plasmonic MoO_{3-x}@MoO₃ nanosheets obtained from surface oxidation of MoO3-x were employed as a surface-enhanced Raman scattering (SERS) substrate for methylene blue detection [1]. MoO₃ also enters the composition of solar cells and light-emitting diodes [2,3]. MoO₃ nanoribbons were proposed as a reversible chemochromic material [4]. Redox active polyaniline-h-MoO₃ hollow nanorods [5], ordered mesoporous α -MoO₃ with iso-oriented nanocrystalline walls [6] and ultrathin MoO₃ nano-crystals self-assembled on graphene nanosheets [7] were proposed as new supercapacitors. It is also applied in the selective conversion of propylene [8]. But MoO₃ is mostly studied for use as an anode material for Li-ion batteries. Recently, singlecrystalline α -MoO₃ nanobelts prepared in 5 M HNO₃ delivered a capacity of 175 mAh g⁻¹ at the first cycle at 2C rate, falling to 150 mAh g⁻¹ after 10 cycles, while commercial MoO₃ delivers a stable reversible capacity of 72 mAh g⁻¹ at 2C rate [9]. To overcome the degradation of MoO₃ nanorod anodes in lithium-ion batteries at high-rate cycling, coating of the nanorods by a protective layer has been proposed. The capacity of α- MoO₃-In₂O₃ coreshell nanorods maintains 1114 and 443 mAh g⁻¹ after 50 cycles at 0.2C and 2C rate, respectively [10]. Conformal passivation of the surface of MoO₃ nanorods by HfO₂ using atomic layer deposition (ALD) was proposed with success [11]. After 50 charge/discharge cycles at high current density1500 mA g⁻¹, HfO₂-coated MoO₃ electrodes exhibited a specific capacity of 657 mAh g⁻¹. MoO₃ nanoparticles were electrodeposited on Ti nanorod arrays that showed enhanced rate capability (300 mAh g⁻¹ at 100 A g⁻¹) and excellent durability (retaining 300 mA h g⁻¹ after 1500 cycles at 20 A g⁻¹) [12]. α-MoO₃/multiwalled carbon nanotube (MWCNT) nanocomposite delivered 490 mAh g⁻¹ at current density 20 A g⁻¹ owing to the high conductivity of the carbon nanotubes [13]. Porous MoO₃ grafted on TiO₂

nanotube array was found to improve the specific capacity with respect to MoO_3 alone and the TiO₂ nanotubes alone by a factor thre [14]. These results show that MoO_3 shows remarkable electrochemical properties for use as an anode for Li-ion batteries. The price to be paid to obtain such performance, however, is the reduction of the size of the particles to the nano-range, and the synthesis of nano-composites. Such synthesis processes, however, are not scalable, and expensive, which explains that the anode of the commercial Li-ion batteries is still graphitic carbon, although much better results are obtained since years at the laboratory scale, not only with MoO_3 but also with silicon and many metal oxides.

MoO₃ usually exists in three main phases: monoclinic, hexagonal and orthorhombic structure, the later being the most thermodynamically stable phase. Orthorhombic MoO₃ (α -MoO₃, n-type semiconductor) attracts interest due to its unique layered structure, which is composed of MoO₆ octahedra in which the Mo atom is surrounded by a distorted oxygen octahedron and connected to another MoO₆ octahedra through edges and corners by covalent and ionic bond, to form double layers [15,16]. The lamellar structure contains extension channels with tetrahedral and octahedral holes suitable for insertion and de-insertion of Li⁺ ions [6]. Crystalline α -MoO₃ has high theoretical discharge capacity of ~370 mAh g⁻¹, based on a 2e⁻ reduction due a wide range of oxidation states from +4 to +6 [17,18]. The electrochemical behavior of α -MoO₃ crystals can be described by the redox reaction:

$$xLi^{+} + MoO_{3} + xe^{-} \leftrightarrow Li_{x}MoO_{3}.$$
 (1)

Several methods have been used to prepare nanostructured molybdenum oxides, i.e. hydrothermal synthesis [19,20] electro-spinning method [21], sol-gel technology [22], thin-film deposition [23]. Ette et al. [24] prepared lamellar α -MoO₃ particles through facile

polymer assisted solvothermal method, and reported good electrochemical performance due to the fast lithium ion diffusion into the lamellar-like morphology.

Non-stoichiometric MoO_{3- δ} oxides with oxygen deficiency [25] are attractive cathode materials for lithium battery application because the excess of metal atoms acts as doping centers, which control the electrical and optical properties [18,26-33]. MoO₃ (Mo as Mo⁶⁺) is insulating and transparent with an electronic conductivity $\sigma < 10^{-8}$ S cm⁻¹ at 25 °C [32], while the conductivity of MoO₂ is $\sigma = 5.0 \times 10^3$ S cm⁻¹ [34]. The poor electrical conductivity of α -MoO₃, due to the almost ideal stoichiometry, is the major drawback, which severely limits the charge transfer during Li insertion. On another hand, the oxygen deficient Mo₄O₁₁ (MoO_{2.75}) exhibits better transport properties with a small electrical resistivity $\rho=10^{-4} \Omega$ cm and larger average lithium chemical diffusion coefficient of ~4×10⁻¹² cm² s⁻¹. In addition, it can accommodate up to 2.1 Li⁺/Mo in its tunnels without change of the lattice providing a theoretical specific capacity of 401 mAh g⁻¹ [27]. However, the reversible capacity becomes stable at the level of 170-200 mAh g⁻¹ [21].

Recent advances to develop highly effective electrode materials for Li batteries derived from composite or blended architectures, which possess at least two percolating frameworks, for ions and electrons [35]. Numerous examples are cited in the literature: $xLi_2MnO_3 \cdot (1-x)LiMn_2O_4$ [36,37], Si/PAN-C [38], $xLiMnPO_4 \cdot (1-x)C-LiFePO_4$ [39], $Li_{1.1}Mn_{1.9}O_4 \cdot LiNi_{0.4}Mn_{0.3}Co_{0.3}O_2$ [40], $LiCoO_2 - LiFePO_4$ [41]. Depending on the nature and the combination of materials, the blending resulted in different advantages such as: (i) inhibition of overheating effects during overcharge conditions, (ii) reduction of the irreversible capacity decay, (iii) improvement of cycling life and (iv) rise of the accessible discharge *C*-rate. In addition to the blends, which are physical mixtures, surface modification has been demonstrated to improve the stability and integrity of cathode particles that complement the blending effect [42].

As an effort to alleviate the fading capacity during cycling of the α -MoO₃ phase, this work present the study of as-grown blend containing stoichiometric MoO₃ and oxygen deficient Mo₄O₁₁ fabricated through a simple heat treatment of MoO₃ coated with zirconia in an inert atmosphere. The Mo_4O_{11} phase of the composite provides better transport properties by solving the problem of the poor electronic conductivity of MoO₃ framework, and by buffering effectively the volume change during cycling. The ZrMo₂O₈ decoration is an effective method to preserve the side reactions occurring at the electrolyte-electrode interface that degrade the electrode performance. The samples are investigated by X-ray powder diffraction (XRD), thermal gravimetric analysis (TGA), scanning electron microscope (SEM) and Raman spectroscopy (RS). The structural analyses show that the composite is formed of stoichiometric MoO₃ and oxygen-deficient phases Mo₄O₁₁+Mo_xO_y. The insertion of lithium into the composite is performed by electrochemical methods and compared with that of pristine MoO₃ and Mo₄O₁₁ hosts. Cyclic voltammetry (CV), galvanostatic and electrochemical impedance spectroscopy (EIS) measurements have shown the enhanced transport properties of the composite electrode at the origin of the improvement of the reversible capacity and rate capability.

2. Experimental

2.1. Synthesis of the composite

Layered MoO₃ (α -MoO₃) was prepared by a citrate sol–gel method using ammonium molybdate tetrahydrate (NH₄)₆Mo₇O₂₄•4H₂O) as precursor. First, a stoichiometric amount of ammonium molybdate was dissolved in de-ionized water to form an aqueous solution, which was added in a second step to an aqueous solution of citric acid with a 1:1 ratio for metal/chelating agent while stirring gently. The pH values was adjusted to pH=7 using ammonium hydroxide. Then, the sol was obtained by stirring the homogenous mixture for 3 h

in order to favor the complex reaction between the metal ion and the chelating agent. The transparent gel was formed after the slow evaporation of the solution heated at 70 °C. Continuous heating with stirring led to the transformation of the gel to a xerogel, which converted to powder by further drying at ca. 120 °C. The resulting dried precursor was ground and calcined at 500 °C for 5 h in air to obtain MoO₃ single crystals (α -MnO₃). The zirconia-coated composite, i.e. oxygen deficient Mo_xO_y, was obtained by mixing α -MnO₃ with Zr(OH)₄ prepared by precipitation of ca. ~4% ZrCl₄ and NaOH dissolved in bi-distilled water. The mixture Zr(OH)₄+(α -MoO₃) was stirred at room temperature for 3 h, then filtrated, and dried overnight at 60 °C. The final stage to obtain oxygen-deficient blend was a calcination under reduced atmosphere at 500 °C for 5 h in a 5% H₂/Ar flow

2.2. Characterization

Thermogravimetric (TG) measurements were carried out using a thermal gravimetric analyzer (Perkin Elmer, TGA 7 series) in the temperature range of 30–1000 °C in air at a heating rate of 10 °C min⁻¹. The structure of the samples was analyzed by X-ray diffraction using a Philips X'Pert apparatus equipped with a CuK_{α} X-ray source ($\lambda = 1.54056$ Å). Data were collected in the 20-range 10–80°. XRD pattern was analyzed by the Rietveld structure refinement program, FULLPROF [43]. The particle morphology of the samples was examined by scanning electron microscope (SEM, JEOL, Japan, JXA-840A). High resolution transmission electron microscopy (HRTEM) analysis was performed using a JEOL TEM2010F at a 200 kV acceleration voltage. For TEM analysis, the powder sample was dispersed on a 3-mm Cu-grid with a hole size of 1 × 2 mm². HRTEM and elemental mapping were completed by high-angle annular dark field in a scanning transmission electron microscope (HAADF/STEM) using Emispec ES vision, version 4.0, of the STEM-EDX mapping system. Raman spectra were collected with a double monochromator (Jobin-Yvon

model U1000) using the 514.5 nm line from the Spectra-Physics 2020 Ar-ion laser. The spectra were recorded using a backscattering geometry and the laser power was kept below 25 mW to prevent the degradation of materials upon data acquisition. All spectroscopic data were collected with a spectral resolution of 2 cm⁻¹.

2.3. Electrochemical tests

Electrode materials were prepared by mixing 80% (w/w) of the active material, 10% (w/w) super C65 carbon (TIMCAL) and 10% (w/w) polyvinylidene fluoride (Solef PVdF 6020 binder, Solvay), in N-methyl-2-pyrrolidone (NMP, Sigma-Aldrich) to get a slurry. A 90 μ m thick film was obtained by coating this slurry on aluminum foil that gives an electrode loading ~7.7 mg cm⁻². This film was dried overnight at 80 °C, then punched out with the diameter of 1.4 cm. Coin-type cells were assembled in an argon-filled glove box using lithium foil (Alfa Aesar) as anode, LP30 (1 mol L⁻¹ LiPF₆ in (1:1) ethylene carbonate (EC) - dimethyl carbonate (DMC) as electrolyte and glass microfiber filters (Whatmann®-GF/D 70 mm Ø) as separator. VMP3 multi-channel potentiostat (Bio-Logic, France) was used to electrochemically characterize the electrodes at 25 °C in the voltage range of 1.5-2.8 V vs. Li⁰/Li⁺ in galvanostatic test and cyclic voltammetry modes.

3. Results and discussion

3.1. Structure and morphology

Fig. 1a shows the X-ray powder diffraction (XRPD) patterns for the as-prepared pure MoO₃ (α -MoO₃) and the decorated MoO₃-Mo₄O₁₁ composite sample synthesized under reduced atmosphere. The XRD spectrum of α -MoO₃ exhibits distinct and sharp peaks attributed to the α -MoO₃ phase indexed in the orthorhombic structure, *Pbnm* space group (JCPDS card 05-

0508). The lattice parameters a=3.993 Å, b=13.575 Å and c=3.713 Å were determined using 12 Bragg lines that are in good agreement with values of the literature [15,16]. The XRD diagram of the composite (blend) material shows complex features with the superposition of three sets of Bragg lines. XRD analysis was carried out by Rietveld structure refinement (Fig. 1b), which matches well with the experimental data and gives the composition of the blend sample. The structural data for the modelling were taken from previously reported articles for α -MoO₃ [15], γ -Mo₄O₁₁ [45] and α -ZrMo₂O₈ [46]. The three phases of low symmetry appear to be with the proportion as follows: (1) an orthorhombic α -MoO₃ (~65 mol.%) (2) an orthorhombic γ -Mo₄O₁₁ (30.2 mol.%) and (3) a trigonal α -ZrMo₂O₈ (4.8 mol.%). Almost no change is observed in the value lattice parameters of the MoO₃ component after inert heattreatment. The appearance of the oxygen deficient oxide MoO_{3- δ} with δ =0.25 is attributed to a slight reduction of MoO₃ in hydrogen containing atmosphere [44] that takes part in creation of oxygen vacancies. The non-stoichiometric molybdenum oxide, Mo₄O₁₁, is clearly detected by the presence of XRD peaks located at 2θ position 20.9, 22.04, 31.9, 34.4 and 48.2°, which match well with database values (JCPDS card 89-6725). The suboxide Mo_4O_{11} can also be written $(Mo_3^{6+}Mo^{4+})O_{11}$ to outline the two valence states of Mo in it. Kihlborg demonstrated its three-dimensional network based on the ReO₃-type structure characterized by the presence of empty channels [25]. The lattice parameters of the γ -Mo₄O₁₁ phase (*Pnma* S.G.) are determined as a=24.397 Å, b=5.443 Å, c=6.732 Å that are in agreement with the data in Ref. 6. Therefore, Mo_4O_{11} can be considered as an intermediate phase during the structural change from MoO₃ to MoO₂ [44]. The third phase characterized by an additional peak at $2\theta = 30.54^{\circ}$ related to trigonal α -ZrMo₂O₈ phase (*P*-3*c* S.G.). The structure of the zirconium molybdate is a two-dimensional network with layers perpendicular to the c axis that is built from ZrO_6 octahedra linked together by MoO₄ tetrahedra with unit-cell parameters a=10.1391 Å and c=11.7084 Å, which match well with the literature data [47]. The presence of α -ZrMo₂O₈

comes from the use of zirconium hydroxide in the synthesis process, which has generated a decoration on the surface of particles. Note that (i) the formation of two molybdate components, i.e. Mo_4O_{11} and $ZrMo_2O_8$ mixed into the blend does alter significantly the lattice parameters of the layered α -MoO₃ phase, (ii) ZrO_2 cannot be detected via XRD and (iii) the overall oxygen deficiency of the blend sample was determine by Raman spectroscopy as shown below.

Fig. 2a shows the gravimetric thermogram and the corresponding differential scanning curve (DTG) of the precursor ammonium heptamolybdate tetrahydrate used as the source of Mo and the citric acid used as the chelating agent for the synthesis of α -MoO₃ by sol-gel method. The thermal behavior in the range 25-950 °C shows stepwise decomposition of the mixture with a total weight loss 71.5 % until the formation of crystalline α -MoO₃ at 550 °C. The large weight loss occurs in two steps: (i) the loss of water (152 °C) and (ii) the loss of ammonia, combustion of carboxylic acid and acetate xerogel (429 °C) [30]. The thermodynamically stable anhydrous α -MoO₃ is formed at T_c ~525 °C, which is in good agreement with reported values [48]. No change in the weight is observed during heating until the melting point of MoO₃ at about 795 °C, followed by the decomposition observed as a broad peak in the DTG curve. Fig. 2b displays the TG curve of the Mo-O blend prepared under reduced atmosphere at 500 °C, recorded in air at a rate 10 °C/min. A pronounced increase of weight is observed at T>580 °C, which is attributed to the oxidation process (gain of oxygen) transforming the blend into the stoichiometric MoO₃ phase at T \approx 600 °C. Upon further heating, we observed the melt at 780 °C followed by the decomposition of the molybdenum trioxide. Here, the fraction 35% of Mo₄O₁₁ is detected from the gain of mass providing the blend composition $0.65MoO_3$ - $0.35Mo_4O_{11}$, a result in agreement with that of Rietveld refinement. Therefore, the presence of a thin ZrMo₂O₈ coating is not detected in TG curve, as expected since its melting temperature is known to be as high as 950 °C.

Fig. 3 presents the SEM images of the α -MoO₃ (a,b) and of the MoO₃-Mo₄O₁₁ blend. The morphology shown in images (3a,3b) reveals well-developed regular slabs of the α -MoO₃ structure with particles composed of dense packed layers. Image 3a presents the MoO₃ slabs, which form terrace at the edge of particles. The surface morphology of blended sample (images 3c,3d) shows different shapes with irregular rod-like particles typically 10 µm thick, decorated with smaller ZrMo₂O₈ particles (~50 nm), which consists of discontinuous lumps attached to the particle surface.

Fig. 4 illustrates typical HRTEM images and HAADF/STEM mapping of Mo-O blend material. The patterns provide evidence for the structural quality of the sample examined. From the HRTEM image (Fig. 4a) crystal defects (marked by red arrows) of a blend particle are identified, which are attributed to the presence of the two Mo-O phases, i.e. the stoichiometric orthorhombic MoO_3 and the oxygen-deficient orthorhombic Mo_4O_{11} phase. The lattice fringes observed in the HRTEM image are an indicative of orthorhombic structure. The measured lattice fringe spacing 0.37(5) nm corresponds to the (001) crystallographic plane of MoO₃. The lattice fringes are not uniform and exhibit some discontinuities or misalignment due to the blend architecture of the particle. To determine the local chemical composition, tomography study of the blend phase is shown in the HAADF/STEM image (Fig. 4b). The image of the representative particle used to obtain the elemental analysis is also shown. The images labeled Mn and O, which represent the elemental mapping of the respective elements, are uniform along the shape of the particle examined. Finally, the STEM image (Fig. 4c) displays the MoO₃-Mo₄O₁₁ particles decorated by ZrMo₂O₈. The lighter part surrounding the darker particles is the ZrMo₂O₈ layer, few nmthick.

Fig. 5 displays the Raman spectra of the α -MoO₃ and MoO₃-Mo₄O₁₁ blend sample. In the high wavenumber region, the Raman bands observed at 776, 848, and 902 cm⁻¹ are the

unique spectral features of the α -MoO₃ orthorhombic phase, especially the 902-cm⁻¹ peak is assigned as the molybdyl mode, which is the vibration of the terminal Mo=O in the layered structure [38]. The deviation from stoichiometry (i.e. the value of *x* in MoO_{3-x}) can be determined from the intensity ratio (I₁₈₅/I₂₉₅) of the Raman bands, i.e. the wagging modes of the terminal Mo=O groups located at 285 and 295 cm⁻¹ as a function of *x* in Fig. 11 of ref. [50]. This deviation from stoichiometry, however is found to be small (the order of 0.5%) for α -MoO₃. The much more oxygen-deficient phase in the blend MoO₃-Mo₄O₁₁ is *x*=6%.. The Raman pattern of the Mo-O blend displays superposition of both MoO₃ and Mo₄O₁₁ components of the blended samples. Seven bands located at 148, 423, 441, 743, 781, 897 and 942 cm⁻¹ are assigned to the internal modes of the orthorhombic Mo₄O₁₁ phase [51]. In addition, small peaks/shoulders pointed out at 177, 326, 360, 751, 885, 943 and 1003 cm⁻¹ reveal the presence of a small amount of ZrMo₂O₈, in good agreement with the XRD results. These Raman peaks are respectively assigned to the lattice mode, the asymmetric and symmetric bending, the asymmetric stretching and the symmetric stretching of MoO₄ tetrahedra [46].

3.2. Electrochemical features

Fig. 6 shows the cyclic voltammograms (CV) of α -MoO₃ (a) and the Mo-O blend (b) samples as positive electrodes in Li coin-type cells. Cycles were performed in the potential range 1.5-3.5 V vs. Li⁰/Li⁺ at a scan rate 0.05 mV s⁻¹. The CV curve of α -MoO₃ (Fig. 5a) in the first cycle shows only one anodic peak at 2.55 V, but two cathodic peaks at potentials of 2.70 and 2.30 V vs. Li⁰/Li⁺. These two reduction peaks correspond to consecutive Li⁺ ion intercalation processes into the MoO₃ framework: (i) onto sites into the interlayer spacing between the [MoO₆] octahedral layers (named van der Waals gap) and (ii) onto sites into the slabs, i.e. octahedral intra-layers [52] as illustrated in Fig. 10 of Ref. [53]. The intercalation process

associated with the peak observed at 2.7 V is irreversible, as it is observed only during the first intercalation reaction; this peak vanishes in subsequent cycles. Tsumura and Ingaki [54] reported the irreversible reaction during the first lithiation, which proceeds in a two-phase reaction up to $Li_{0.25}MoO_3$. The appearance of the α -MoO₃/Li_xMoO₃ system causes a pronounced expansion of the interlayer spacing [55]. The first cycle CV curve for the MoO₃-Mo₄O₁₁ blend (Fig. 5b) appears to be more complex showing the superposition of redox peaks due to each component. The three peaks of MoO₃ are observed at the same potentials as in the parent material, while three sets of additional peaks are attributed to the Mo₄O₁₁ phase: (i) the reversible cathodic peaks at 3.28 and 1.91 V, (ii) reversible anodic peaks at 3.33 and 1.88 V and (iii) irreversible cathodic peaks at 2.45 and 2.20 V vs. Li^0/Li^+ . These redox peaks assigned to Mo₄O₁₁ are in good agreement with data reported by Besenhard and Schollhorn [56], who noticed trace of reduced Mo suboxide during the reduction process of molybdenum trioxide.

Fig. 7 presents the galvanostatic discharge–charge profiles of the Li coin-type cells cycled at C/10 rate for 50 times, while Figs. 8 (a-b) display the electrochemical performances of Mo-O electrodes. In the first discharge process (lithium intercalation), the discharge–charge curves for α -MoO₃ (Fig. 7a) and MoO₃-Mo₄O₁₁ blend (Fig. 7b) show two plateaus that correspond to the redox reaction recorded in CV curves. The first irreversible plateau corresponds to an irreversible capacity of ~50 mAh g⁻¹. It is observed at about 2.75 V *vs.* Li⁰/Li⁺ and vanishes in the second and forthcoming cycles. This suggests that part of the Li⁺ ions, first introduced during the reduction reaction (discharge), cannot be extracted. Such an effect has also been observed in V₂O₅ [57]. Thus the total intercalation process up to 1.5Li⁺/Mo can be described as the formation of three phases separated by the bi-phase domain MoO₃-Li_{0.25}MoO₃ that is responsible for voltage plateaus in the first discharge at 2.7 V. The charge-discharge profiles of the Li cell with the MoO₃-Mo₄O₁₁ positive electrode

shows multiple stepwise plateaus at different voltages, associated to the different site occupancies for Li⁺ ions into the framework of each component of the blend. These curves are in good agreement with the data of the cyclic voltammetry. The specific capacity of the α -MoO₃ in the first discharge is 250 mAh g⁻¹ and decreases to ~100 mAh g⁻¹ at the 50th cycle, which represents a capacity retention of 37% at rate C/10 (see Figs 7 and 8). The presence of the Mo_4O_{11} phase in the blend improves significantly the electrochemical performance of the electrode. The specific capacity is raised to 275 mAh g^{-1} at the first cycle, 135 mAh g^{-1} after the 50th cycle, both of them being higher than for the MoO₃ electrode. Our results can be compared with those reported for polyaniline (PANI)/MoO₃ nanobelt composites synthesized by a hydrothermal method, which exhibited an initial specific capacity 228 mAh g^{-1} , but only ~90 mAh g^{-1} after 40 cycles at a current density of 30.7 mA g^{-1} (~C/12 rate) [58]. The rate capability presented by the modified Peukert plots (Fig. 8a) for the 2nd cycle (after the cell formation process and avoid the irreversible loss of capacity associated to the vanishing of the plateau at 2.7 V in Fig. 7) confirms the enhancement in the discharge specific capacity at high C-rate for the MoO₃-Mo₄O₁₁ blended electrode. Typically, at a rate of 2C the capacity is twice that of pure MoO₃; the MoO₃-Mo₄O₁₁ blend electrode retains a capacity of 118 mAh g^{-1} against 60 mAh g^{-1} for the pure MoO₃ cathode material.

Fig. 9 presents the EIS results for the $MoO_3-Mo_4O_{11}$ blended electrode compared with the pristine MoO_3 material, measured in the frequency range 100 kHz-0.1 Hz with a 5 mV bias. These Nyquist plots show clearly the enhanced transport property of the composite electrode including the Mo_4O_{11} phase. Figs. 9 (a-b) display the electrochemical performances of Mo-O electrodes. This increase in the discharge capacity is attributed to the enhancement of the electronic conductivity of the electrode materials, which can accept higher current densities. These results support the advantage of the Mo-O blend containing the Mo_4O_{11} phase. Stoichiometric MoO_3 is an insulator with a band gap of 3.1 eV. Oxygen vacancies acts

as doping centers and restores a semiconducting behavior with a conductivity that, however, remains small in MoO_{3-δ}. On another hand, Mo₄O₁₁ is a metal (resistivity 1.66 $10^{-4} \Omega$ cm) [59]. Since Mo₄O₁₁ can be viewed as MoO₃ that has lost ¹/₄ oxygen per chemical formula, the metallic character of Mo₄O₁₁ can be viewed as the result of an insulator to metal Mott transition associated to the increasing concentration of oxygen vacancies. The increase of the electrical conductivity in the blend, as evidenced in Fig. 8, simply gives evidence that the Mo₄O₁₁ phase forms an electric conductive network. The increased conductivity and the access to the oxidation states +6, +5 of Mo due to Mo₄O₁₁ explains the improvement of the rate capability at C>0.2 in the blend evidenced in Fig. 8b. The better cycling stability can be attributed to the combination of two effects: (a) the increase of electronic conductivity also makes possible the extraction of a larger amount of lithium. (b) the buffering effect of the non-stoichiometric Mo₄O₁₁ component into the blend. (c) the presence of the ZrMo₂O₈ decoration protects the electrode from side reaction at the electrolyte-electrode interface.

To our knowledge, this blend is the best result published for molybdenum oxide micronsized particles so far. As usual better results can be obtained by decreasing the size of the particles to the nano-range. In particular C-MoO₃ porous nanofibers, could deliver a stable reversible capacity of circa 200 mAh g⁻¹ [21]. This performance, however, is due to the contribution of the carbon to the electrochemical process, and also the contribution of active sites at the porous surface, evidenced by the fact that the capacity at the first cycles was much larger than the theoretical value. Similar remarkable improvements of the electrochemical properties have been obtained by decreasing the size of $ZrMo_2O_8$ -coated particles, such as ZrO_2 -coated Li₄Ti₅O₁₂ anodes [60], or ZrO_2 -coated LiMn₂O₄ cathodes [61]. The drawback is that such nano-structures have a low density, and their synthesis process is also less scalable than the simple sol-gel process. Nevertheless, the present results suggest that decreasing the size of the $ZrMo_2O_8$ -decorated MoO₃-Mo₄O₁₁ blend to the nano-range might be promising for applications as electrode of lithium-ion batteries.

4. Conclusions

In this work, we have investigated the structural and electrochemical properties of a blend electrode prepared by self-synthesis of molybdenum oxides creating a suboxide component, which enhances the properties of the physical mixture. The synthetic procedure performed in inert atmosphere with addition of Zr(OH)₄ provides particles decorated with nanometric zirconium molybdate particles. The structure and morphology of samples were characterized by XRD, TGA, SEM, HRTEM, HAADF/STEM mapping and Raman analyses that show a blend composition 0.65MoO₃-0.35Mo₄O₁₁ decorated with ZrMo₂O₈ nanoparticles. It is found that both components of the blend are electrochemically active, providing an initial discharge capacity of ~282 mAh g⁻¹ in the voltage range 1.5-2.8 V vs. Li^0/Li^+ larger than that of α -MoO₃. We have shown that blending cathode materials results in the minimization of the shortcomings of the parent material, MoO₃. We solved the problem of the poor electronic conductivity of MoO₃ by the fabrication of a Mo-O composite including an oxygen deficient MoO_{3- δ} (δ =0.25) component. Due to the oxygen vacancies, which act as doping centers, the $MoO_{3-\delta}$ phase forms an electric conductive network so that the electrochemical performance is enhanced at high C rates. Therefore, the improved electrochemical properties in the MoO₃- Mo_4O_{11} cell is attributed to two factors: (i) the presence of oxygen vacancies in the Mo_4O_{11} phase that enhances the electrical conductivity of the blend and serves as buffering component to absorb the volume expansion and (ii) the $ZrMo_2O_8$ -decoration that preserves the electrode against side reaction with the electrolyte.

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Figure captions

Fig. 1. (a) X-ray powder diffraction for pure MoO_3 prepared by sol-gel method and zirconia coated composite calcined in reduced atmosphere. (b) Rietveld refinement of the XRD data of the ZrMo₂O₈ decorated MoO₃-Mo₄O₁₁ composite.

Fig. 2. (a) TGA and DTG curves of the precursor showing the crystallization and decomposition of α -MoO₃ in air with heating rate 10 °C/min. (b) TGA curve of the blend MoO₃-Mo₄O₁₁ showing the oxidation of the suboxide component at 580 °C.

Fig. 3. SEM images of α -MoO₃ (a,b) and MoO₃-Mo₄O₁₁ blend decorated by ZrMo₂O₈ (c,d).

Fig. 4. (a) HRTEM image of Mo-O blend material showing the crystal defects (marked by red arrows) that are induced by the presence of stoichiometric MoO_3 and oxygen-deficient Mo_xO_y phases in the particle. (b) HAADF/STEM mapping and (c) STEM image showing the ZrMo₂O₈ phase surrounding the core of blend Mo-O particles.

Fig. 5. Raman spectra of the orthorhombic α -MoO₃ and ZrMo₂O₈-decorated Mo-O blend. Samples were excited at a laser wavelength of 514.5 nm.

Fig. 6. Cyclic voltammograms of α -MoO₃ (a) and MoO₃-Mo₄O₁₁ blend (b) recorded at 0.05 mV s⁻¹ in the potential range 1.5-3.5 V vs. Li⁰/Li⁺ in Li cell using 1 mol L⁻¹ LiPF₆ in EC:DEC electrolyte.

Fig. 7. Charge-discharge profiles as a function of cycles of Li coin-type cells including (a) α -MoO₃ and (b) MoO₃-Mo₄O₁₁ blend as cathode materials. Measurements were carried out at C/10 rate in the voltage range 1.5-2.8 V vs. Li⁰/Li⁺.

Fig. 8. Electrochemical performance of Li cells with α -MoO₃ and MoO₃-Mo₄O₁₁ blend electrodes: (a) rate capability at the second cycle (the rate is denoted C/n, where C is the theoretical cathode capacity and a full discharge occurs in n hours) and (b) cycling performance at rate C/10.

Fig. 9. Nyquist plots of (a) α -MoO₃ and (b) MoO₃-Mo₄O₁₁ blend as cathode materials. Measurements were carried out in the frequency range 100 kHz-0.1 Hz with a 5 mV bias. Values are frequencies in Hz.

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Figure 9. Nyquist plot of including (a) α -MoO₃ and (b) MoO₃-Mo₄O₁₁ blend as cathode materials. Measurements were carried out in the 100 kHz-0.1 Hz frequency range with a 5 mV bias.

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Highlights

- Oxygen deficient Mo_xO_y materials were synthesized by a citrate sol-gel method.
- The as-prepared materials exhibit an integrated-type blend structure decorated with α -ZrMo₂O₈ nanoparticles.
- Electrochemical features show the redox peaks attributed to distinct Li⁺-ion insertion/extraction reactions in the MoO₃ and Mo₄O₁₁ hosts.
- Cyclic performance revealed improved reversibility and electrochemical stability of the composite.