

Supplementary Information for:

Electrochemical preparation of porous MoO₃ film with a high rate performance as anodes for lithium ion batteries

Guangyu Zhao^b, Naiqing Zhang^{a,b} and Kening Sun^{a*}

^a State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin, Heilongjiang 150090, PR China

^b Academy of Fundamental and Interdisciplinary Sciences, Harbin Institute of Technology, Harbin, Heilongjiang 150080, PR China

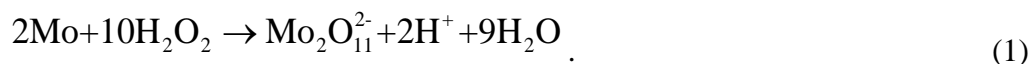
Corresponding author: Tel/Fax: +86 451 86412153.

E-mail address: keningsun@yahoo.com.cn (K. Sun).

Experimental section

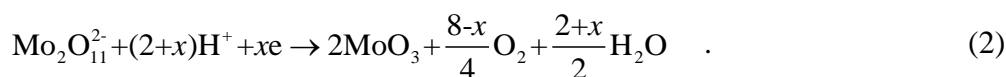
Preparation of porous MoO₃ film

All chemical reagents were of analytical grade and were obtained commercially. A CHI 660D electrochemical workstation was used for electrodeposition. The acid peroxy-polymolybdate electrolyte was prepared by dissolving 3.0 g Mo powder (2 μm, Aladdin Chemistry) in 100 mL H₂O₂ at 60 °C following the reactions:



When the metal powder was completely dissolved and the exothermic reaction had ended, a Pt foil was added to reduce the excess peroxide. Then the solution was neutralized to be neutral with ammonia. The MoO₃ film was electrodeposited at room temperature with a

constant reduction current of 1 mA using 154 mm² circular Ni foam, a Pt foil and a saturation mercury electrode (SCE) as the working, counter and reference electrodes, respectively. The electrochemical reaction followed Formula 2.¹ The as-deposited samples were heat-treated at 400 °C in Ar atmosphere for 3 h.



For comparison, MoO₃ powder were prepared using acid inducing deposition method which was realized by adjusting sodium molybdate solution to acid.² The as-prepared MoO₃ powder was also heat-treated at 400 °C in Ar atmosphere for 3h.

Structural and electrochemical characterization

A field-emission scanning electron microscope (Hitachi, Su-8100) was used to obtain scanning electron microscope (SEM) images. High resolution transmission electron microscope (HRTEM) images, selected area electron diffraction (SAED) patterns and energy dispersive X-ray spectra (EDS) patterns were obtained on a FEI Tecnai G². X-ray photoelectron spectra (XPS) were obtained with a K-Alpha electron spectrometer from Thermofish Scientific Company using Al K α (1486.6 eV) radiation. The base pressure was about 1 \times 10⁻⁸ mbar. The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon. X-ray diffraction (XRD) patterns were obtained by Rigaku D/max-2000 X-ray diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). Particle size analysis of MoO₃ powder prepared using acid inducing deposition method was done with a laser particle size analyzer (OMECA, LS 900). The mass of the electrodes were quantified by a Mettler AE240 balance.

A PAR 2273 electrochemical workstation was used for the cyclic voltammetry (CV) and

electrochemical impedance spectroscopy (EIS) measurements. The battery tests were carried out in the CR2025 button testing batteries consisting of a porous MoO₃ film electrode, microporous membrane (Celgard 2400) and lithium foil as the counter electrode. For comparison, pristine MoO₃ powder electrodes with area of 154 mm² coated on Cu foils were used for electrochemical measurements (MoO₃ powder: polyvinylidene fluoride (PVDF): acetylene black=8:1:1, weight ratio). The electrolyte was LiPF₆ (1M) in a 50: 50 (V/ V) mixture of ethylene carbonate (EC) and diethyl carbonate (DMC) provided by Tinci Company (Guangzhou China). A BTS-2000 Neware Battery Testing System was employed for charge/discharge testing in the voltage range of 3.0–0.02 V vs. Li⁺/Li.

[1]. T. M. McEvoy, K. J. Stevenson, J. T. Hupp and X. Dang, *Langmuir*, 2003, **19**, 4316–4326.

[2]. R. Zheng, E. Wang, *Chem. Online*, 1984, **9**, 12–15.

SI-1. Size distribution curve

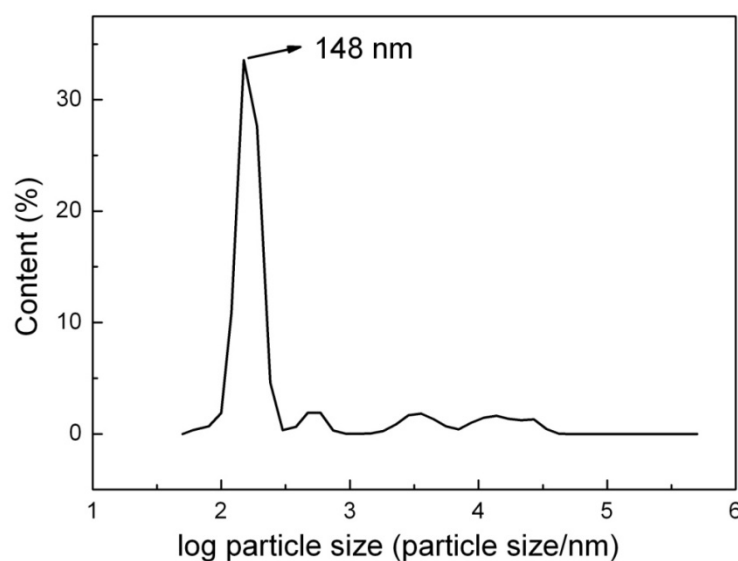


Figure S1 Size distribution curve of pristine MoO₃ powder for comparison.

SI-2. TEM results

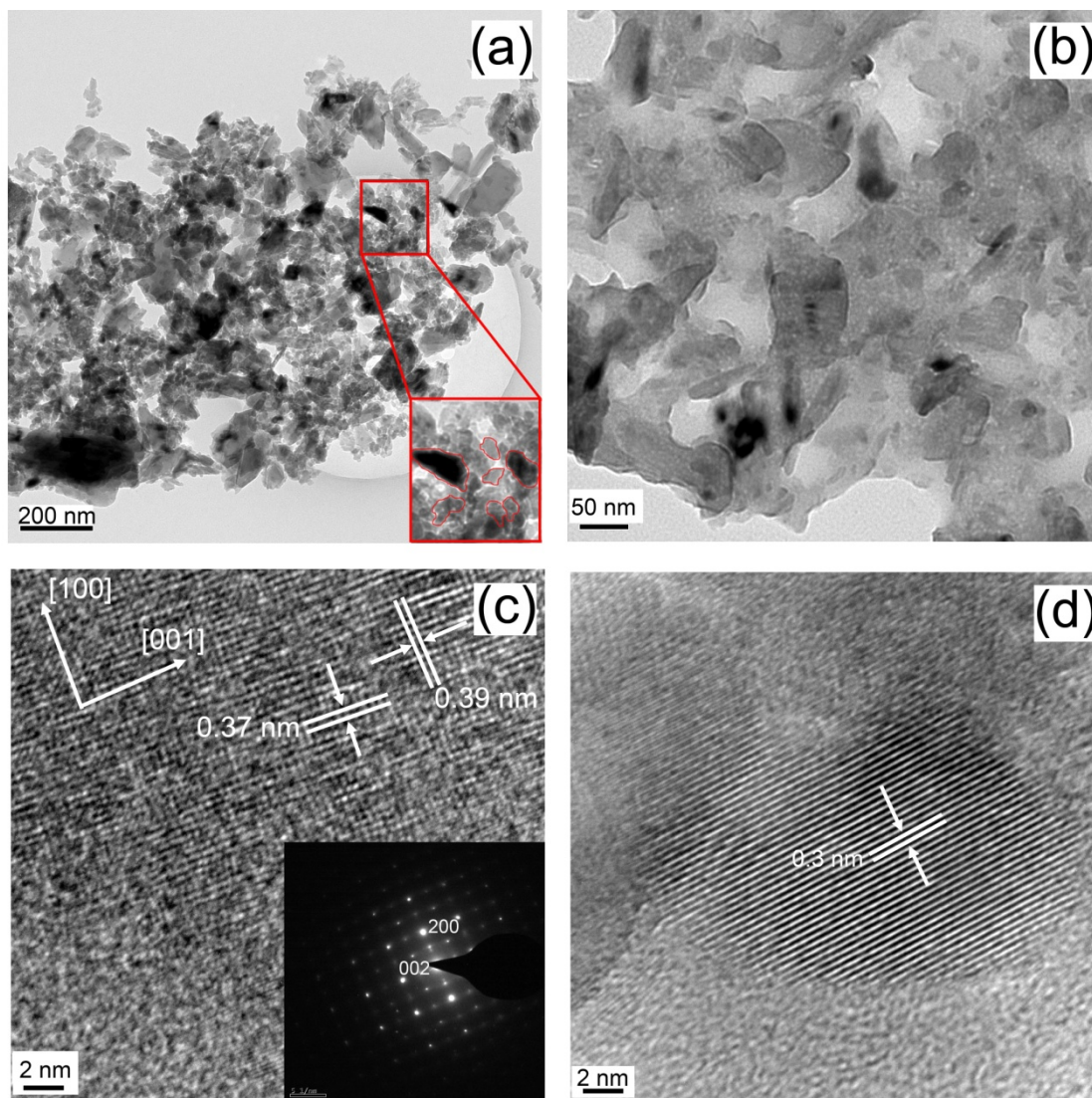


Figure S2 (a, b) TEM images of MoO_3 grains; (c, d) HRTEM images of the MoO_3 grains (insert in (c) is the SAED pattern).

SI-3. XRD patterns

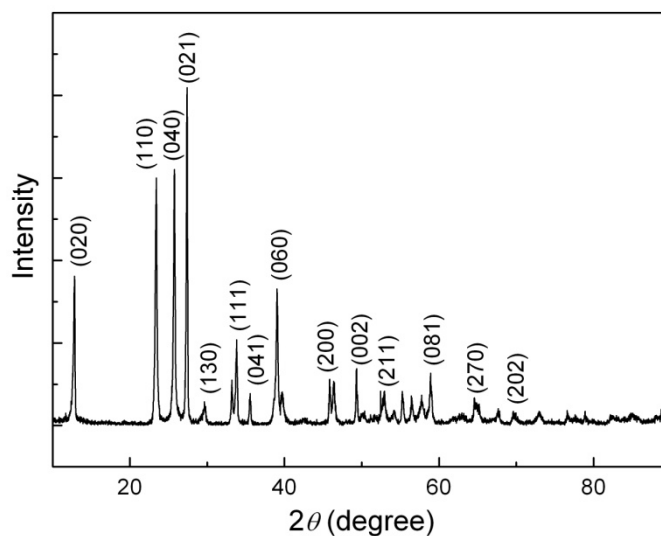


Figure S3 XRD patterns of the MoO_3 grains scratched from porous film.

SI-4. EDS patterns

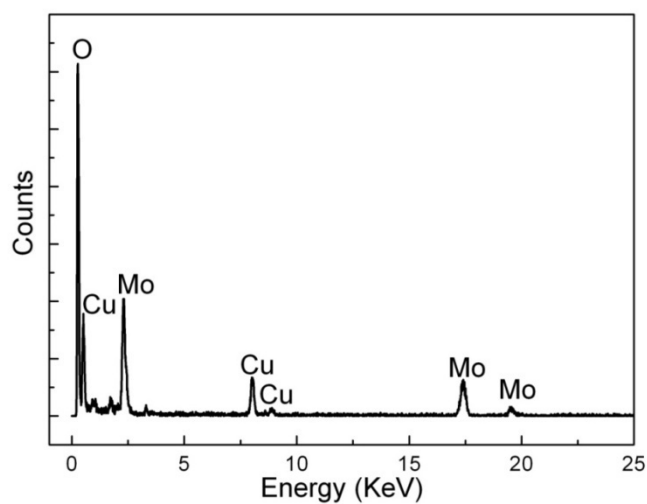


Figure S4 EDS patterns of MoO_3 grains scratched from porous film.

SI-5. XPS spectra

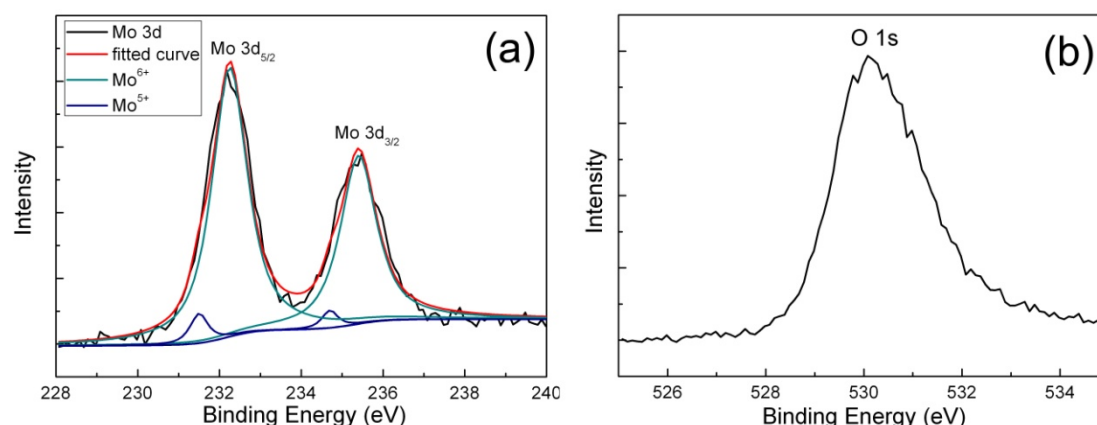


Figure S5 High resolution XPS spectra (Mo and O elements) of porous MoO₃ film.

SI-6. EIS tests

The diffusion coefficients are calculated according to the following equation³⁻⁵:

$$\sigma = \left[\frac{RT}{\sqrt{2}n^2 F^2 AC_{\text{Li}}} \right] \frac{1}{\sqrt{D_{\text{Li}}}}, \quad (3)$$

converted to

$$D_{\text{Li}} = \frac{R^2 T^2}{2n^4 F^4 A^2 \sigma^2 C_{\text{Li}}^2}, \quad (4)$$

where the meanings of n is the number of electrons per-molecule during oxidization, A is the surface area of the anode, D_{Li} is the diffusion coefficient of lithium ion, R is the gas constant, T is the absolute temperature, F is the Faraday constant, C_{Li} is the concentration of lithium ion, and σ is the Warburg factor which has relationship with Z_{re} :

$$Z_{\text{re}} = R_{\text{D}} + R_{\text{L}} + \sigma \omega^{-1/2}, \quad (5)$$

where the meanings of Z_{re} is the real part of the resistance in the low frequency region, ω is corresponding frequency. Fig. S7† shows the relationship between Z_{re} and square root of

frequency ($\omega^{-1/2}$) in the low-frequency region.

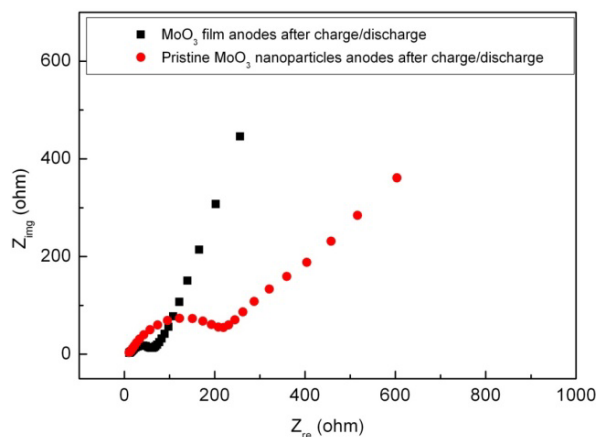


Figure S6 Nyquist plots of porous MoO₃ film anodes and the pristine MoO₃ powder anodes after multi-cycle charge/discharge.

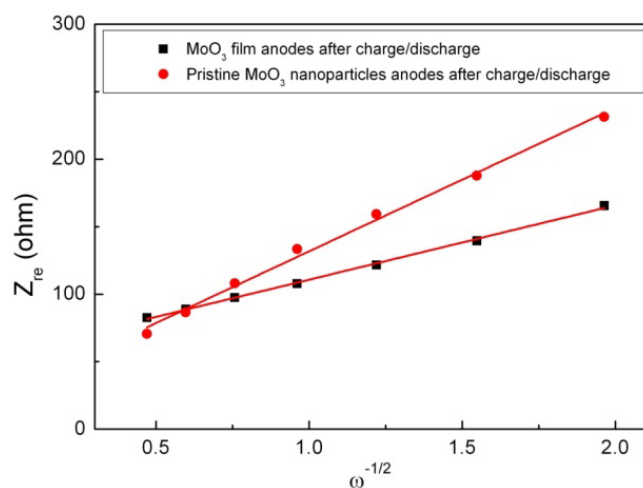


Figure S7 Relationship between real part of the resistance (Z_{re}) and square root of frequency ($\omega^{-1/2}$) in the low-frequency region.

[3]. N. Takami, A. Satoh and M. Hara, *J. Electrochem. Soc.*, 1995, **142**, 371–378.

[4]. H. Liu, C. Li, H. P. Zhang, L. J. Fu, Y. P. Wu and H. Q. Wu, *J. Power Sources*, 2006, **159**, 717–720.

[5]. A. J. Bard and L. R. Faulkner, in *Electrochemical Methods*, Wiley, New York, 1980, p. 213.