## Supporting Information

## Rationally confining molybdenum based nanodots in porous carbon for highly reversible lithium storage

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## I. Experimental section

**Material synthesis:** For the molten salt synthesis of Mo-based carbon composite, 0.7 g of molybdenyl acetylacetonate [MoO<sub>2</sub>(acac)<sub>2</sub>] was ground with 7 g of zinc chloride (ZnCl<sub>2</sub>) powder. During the grinding process, water in the air is absorbed to form a saffron paste. The paste was transferred to a quartz boat with a cover and pre-heated at 110 °C for 2 h in a pure Ar atmosphere to remove any water. Then, the furnace temperature was increased from 110 °C to 600 °C at a heating rate of 2 °C min<sup>-1</sup> and was held at that temperature for 2 h. The furnace was naturally cooled down to room temperature, and the obtained black powder was washed with 1 M hydrochloric acid (HCl) solution and de-ionized water 2-3 times and was then vacuum filtered. Finally, the product was dried and named ZMC-Ar.

The synthesis was performed in a similar fashion by changing the calcination atmosphere from pure Ar to 10% H<sub>2</sub>/Ar, and the resulting sample was named ZMC-H<sub>2</sub>.

For comparison purposes, a sample without ZnCl<sub>2</sub> molten salt, which was directly calcined in an Ar atmosphere, was also prepared and named MC-Ar.

**Characterization:** The sample microstructures were characterized using fieldemission scanning electron microscopy (FE-SEM, Hitachi S-4800, Japan) and transmission electron microscopy (TEM, FEI Tecnai G2T20, America). The corresponding bright-field STEM images and EDX mapping were obtained using a FEI Tecnai G2F30 S-TWIN field emission transmission electron microscope equipped with EDAX energy-dispersive X-ray spectroscopy. The crystal structure of as-prepared samples was characterized using X-ray diffraction (XRD) with an X-ray diffraction system (Rigaku Smart Lab Intelligent X-ray, Japan) with filtered Cu K $\alpha$  radiation at 40 kV and 40 mA at room temperature. The nitrogen adsorption–desorption isotherm was tested using a BELSORP-MAX (Japan) instrument at the boiling point of liquid nitrogen. The specific surface area was calculated based on the Brunauer-Emmett-Teller (BET) equation, and the corresponding pore size distribution was measured from the adsorption branch of the isotherm using the Barrett-Joyner-Halenda (BJH) method. Thermogravimetric (TG) analysis was performed using a thermobalance (STA 449 F3 Jupiter<sup>®</sup>, NETZSCH, Germany). X-Ray fluorescence (XRF, ARL ADVANT'XP, America) was used to analyse the elemental composition of samples, along with the inductively coupled plasma mass spectrometry (ICP-MS, PE Optima 2000DV, Germany) using the quantificational digestion of metal oxide in the sample with hot nitric acid.

Electrochemical measurement: To prepare the electrodes for lithium ion batteries, the electrode composed of 80 wt% active materials, 10 wt% carbon black (Ensaco 350G) and 10 wt% binder (Polyvinylidene Fluoride, PVDF) was slurry-coated onto a copper foil with N-methyl-2-pyrrolidone (NMP) as a solvent. Then, the electrode was dried at 100 °C for 12 h in a vacuum oven. The mass loading of active material is 1.0-1.3 mg cm<sup>-2</sup> for both ZMC-H<sub>2</sub> and ZMC-Ar samples. CR2025-type coin cells were used to evaluate the electrochemical performance of samples with metallic lithium foil and microporous polypropylene film (Celgard 2400) as the counter electrode and separator, respectively. The electrolyte comprised 1 M LiPF<sub>6</sub> dissolved in a 1:2 (by volume) mixture of ethylene carbonate (EC) and dimethyl carbonate (DEC) with 10 wt% ethyl methyl carbonate (EMC) as an additive. The cells were assembled in an argon-filled glove box. A galvanostatic discharge-charge test was performed between 0.01 and 3.0 V using a NEWARE BTS computer-controlled galvanostat (Shenzhen, China). Cyclic voltammetry was performed on a Princeton Applied Research (PARSTAT 273A) advanced electrochemical system. Electrochemical impedance spectroscopy (EIS) was obtained in the frequency range of 100 kHz - 0.01 Hz with a 10 mV alternating current potential bias using a Solartron 1260 frequency response analyzer in combination with a Solartron 1287 potentiostat.

## **II. Supplementary Results**



Fig. S1 SEM images of the samples obtained at different molten salt synthesis atmosphere, (a, b) ZMC-Ar, and (c, d) ZMC-H<sub>2</sub>.



Fig. S2 STEM-EDX line scan image of ZMC-Ar sample.



Fig. S3 XRD pattern of the ZMC-Ar sample.



Fig. S4 XRD pattern of the MC-Ar sample.



Fig. S5 SEM images of the sample (MC-Ar) obtained without ZnCl<sub>2</sub> molten salt under Ar atmosphere.



Fig. S6 Raman spectrum of ZMC-Ar nanocomposite.



Fig. S7 Nitrogen adsorption-desorption isotherm of ZMC-Ar sample, inset is the corresponding pore size distribution plot based on the adsorption branch.

Samples	$\frac{S_{BET}{}^{[a]}}{[m^2 g^{-1}]}$	Total Pore volume <sup>[b]</sup>	Mesopore volume <sup>[c]</sup>	Mesopore volume ratio
MC-Ar	17	0.025	0.02	[ <b>v</b> mes/ <b>v</b> total] 80%
ZMC-Ar	257	0.58	0.55	94.8%
ZMC-H <sub>2</sub>	158	0.13	0.08	61.5%

Table S1 BET analysis results of the samples synthesized under different calcination conditions.

[a] Specific surface area calculated from the Brunauer–Emmett–Teller (BET) equation.

[b] Total pore volume measured at  $P/P_0=0.99$ .

[c] Mesopore volume calculated using the BJH method.



Fig. S8 TG analysis of ZMC-Ar and ZMC-H<sub>2</sub> sample under air flow from room temperature to

700 °C.



Fig. S9 XPS survey spectrum of ZMC-H<sub>2</sub> sample.



Fig. S10 A magnified viewing area of HR-TEM image in Fig. 1e.



Fig. S11 The cycling performance of ZMC-H<sub>2</sub> electrode at different current densities.



Fig. S12 Discharge-charge curves of different cycles for the (a) MC-Ar, (b) ZMC-Ar and (c)  $ZMC-H_2$  electrodes at a current density of 500 mA g<sup>-1</sup>.



Fig. S13 Electrochemical impedance spectra of (a) ZMC-Ar and (b) ZMC-H<sub>2</sub> electrodes at

different cycling numbers (tested at 0.5 V in the discharge status).



Fig. S14 TEM images of (a, b) ZMC-Ar and (c, d) ZMC-H<sub>2</sub> electrodes after 300 discharge-charge cycles.