Supporting Information

Aerogel Constructed by Ultrasmall Mn-doped Silica Nanoparticles for Superior Lithium-Ion Storage

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Experiments and simulations

1. Preparation of samples

For the preparation of Mn-doped ultrasmall SiO₂/graphene aerogel (MSGG), 24 mL tetraethyl orthosilicate (TEOS) was added into 18 g ethanol and stirred for 10 min to obtain solution A. Then the HCl (8.4 mL, 1 g/L), MnCl₂ (0.62 g) and graphene oxide (GO) slurry (3 mL, 1 wt% solid content) were added into solution A to obtain solution B. Finally, 6 mL aqueous ammonia (3.6 g/L) was added into solution B with violent stirring to obtain Mn-doped SiO₂/GO hydrogel. The hydrogel was washed several times with water and alcohol alternately. Next, the hydrogel was aged for 10 hours in a mixture of water and alcohol (1:1) at 55 °C. The aged hydrogel was freeze-dried to obtain aerogel A, and the aerogel A was annealed at 500 °C with Ar atmosphere for 3 h to obtain the MSGG.

For the preparation of the Mn-doped SiO₂ aerogel (MSG), the GO slurry was not

added. For the preparation of SiO₂ aerogel (SG), the GO slurry and MnCl₂ were not added.

2. Characterizations

X-ray diffraction (XRD) patterns and X-ray photoelectron spectra (XPS) spectra were recorded on EMPYREAN and XSAM800 spectrometer, respectively. The morphology and structure were observed on JSM-7500F scanning electron microscope (SEM) and JEM-2100F transmission electron microscope (TEM). The thermogravimetric (TG) curve was measured on the TGA/DSC2 thermal analysis system in the air. The element content was tested by the Agilent 5110 inductively coupled plasma optical emission spectrometer (ICP-OES). The electron paramagnetic resonance (EPR) spectra were tested on the JES-FA200 spectrometer. The specific surface area and pore distribution of samples were analyzed by the ASAP2460 automatic physical adsorption instrument.

For the preparation of electrodes, the active materials (SG, MSG and MSGG) were mixed with styrene-butadiene latex (SBL) and super P with a weight ratio of 73%:18%:9%, and the loading mass of active materials was ~3 mg (~1.9 mg cm⁻²). The mixtures were cast on carbon paper by the slurry method. Finally, the electrodes were assembled in CR2032 coin-type cells using the lithium-metal as the counter electrode. The porous morphology of carbon paper is shown in **Figure S1(a)**. Celgard 2500 (polypropylene) was used as the separator. For the electrolyte, 1M LiPF₆ was dissolved into the mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and ethyl methyl carbonate (EMC) with the volume ratio of 1:1:1. The discharge/charge measurements were performed on the CT2001A battery testing system from 0.01 to 2 V. The electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) curves were obtained on the CHI660E electrochemical workstation. For the galvanostatic intermittent titration technique (GITT) measurements, the current pulse of 0.2 A/g was applied for 270 s while the followed relaxation time was 1080 s.

3. DFT simulations

The spin-polarized density functional theory (DFT) calculations were conducted with the Cambridge sequential total energy package (CASTEP), using the Perdew–Burke– Ernzerhof (PBE) generalized gradient approximation (GGA) functional and Gimme's scheme to describe the van der Waals (vdW) force. For the setting of CASTEP, the convergence criteria (energy cutoff of 500 eV, total energy tolerance of $\leq 2 \times 10^{-5}$ eV and force difference of ≤ 0.05 eV/ Å) were set. To save the calculation cost, the model of α -SiO₂ was used. The U=2 for Mn 3d orbitals was set. [1] The 4 × 4 × 4 Monkhorst-Pack grid k-points was used for the calculations. To obtain the energy barrier, the linear synchronous transition/quadratic synchronous transit (LST/QST) tools were employed.

[2]



Figure S1. (a) Morphology of carbon paper. (b) Survey XPS spectra of the three samples. Mn 2p spectrum for (c) SG and (d) MSG. (e) Si 2p spectra for the three samples.



Figure S2. Photographs of **(a)** SiO₂ hydrogel, **(b)** Mn-doped SiO₂ hydrogel and **(c)** Mn-doped SiO₂/GO hydrogel.



Figure S3. SEM morphology of the SG ((a)-(b)) and MSG ((c)-(d)) at different magnifications.



Figure S4. (a) SEM morphology and corresponding EDS elemental mapping images of (b) Si, (c) O and (d) Mn in the MSG.



Figure S5. TEM morphology of (a) SG, (b) MSG and (c) MSGG.



Figure S6. CV curves of the three electrodes at the scanning rate of 0.2 mV/s.



Figure S7. Voltage-capacity curves of (a) SG, (b) MSG and (c) MSGG.



Figure S8. (a) EIS plots, (b) Z_{re} vs. $\omega^{-1/2}$ plots and (c) the corresponding Li⁺ diffusion coefficients of the three electrodes.



Figure S9. Ionic radii of (a) O, (b) Mn and (c) Si. (data from http://abulafia.mt.ic.ac.uk)



Figure S10. Schematic illustration of Mn doping to increase electronic conductivity.

Note: E_g is bandgap, E_c is conduction band and E_v is valence band.

Calculation of specific capacity retention (SCT) value:

Based on Figure 3(a), the SCT values are calculated by Eq. S1.

$$SCT = \frac{C_x}{C_{0.2}} \times 100\% \tag{S1}$$

where, $C_{0,2}$ and C_x represent the average specific capacities at current densities of 0.2 and x A/g, respectively.

Calculation of Li⁺ diffusion coefficient:

The Li⁺ diffusion coefficient can be deduced from the following Eq. S2 and S3.

$$z_{re} = R_1 + R_2 + R_3 + \sigma \omega^{-1/2}$$
(S2)

$$D_{Li} = \frac{R^2 T^2}{2n^4 A^2 F^4 C_{Li}^2 \sigma^2}$$
(S3)

where Z_{re} , σ , ω , D_{Li} , R, T, n, A, F and C_{Li} , represent the real part of the impedance, Warburg factor, angular frequency (ω =2 π f), Li⁺ diffusion coefficient, gas constant, absolute temperature, electrode electrochemical active area, reaction electron number, Faraday's constant and Li⁺ concentration, respectively. The values of σ can be determined from the slope of Z_{re} vs. $\omega^{-1/2}$.

Equation S4:

$$D = \frac{4}{\pi \tau} \left(\frac{m_B V_M}{M_B S}\right)^2 \left(\frac{\Delta E_{\tau}}{\Delta E_s}\right)^2 \tag{S4}$$

Where D is diffusion coefficient; m_B and M_B are the active mass and molar mass of the electrodes, respectively; V_M is the molar volume; and S is the total interfacial area between the electrolyte and the electrode.

Calculation of adsorption energy:

The adsorption energy (E_{ad}) is calculated by Equation S5.

$$E_{ad} = E_{bulk+Li} - E_{bulk} - E_{Li} \tag{S5}$$

where $E_{bulk+Li}$, E_{bulk} and E_{Li} are the energy of a Li^+ in hosts, hosts and a Li^+ .

Weight, m₀ Volume, V₀ Concentration, Co Content, C_x Content, W Samples (g) (mL) (mg/L)(mg/kg) (%) 1 0.0292 25 3.72 3184.9 0.32% 2 0.0292 25 3.77 3227.7 0.32%

Table S1. Experimental details of the ICP-OES tests.

Table S2.	Energies f	or various	configurations.
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Configuration	Energy / eV	
SiO ₂	-8432.0	
Mn-SiO ₂	-11117.7	
Mn-OV-SiO ₂	-10675.3	
Mn-SiO ₂ +Li ⁺	-11323.3	
Mn-OV-SiO ₂ +Li ⁺	-10882.1	
Li ⁺	-201.0	

References

[1] Gallegos, M.; Luna, C.; Peluso, M.; Damonte, L.; Sambeth, J.; Jasen, P. Effect of Mn in ZnO Using DFT Calculations: Magnetic and Electronic Changes. *J. Alloy Compd.* **2019**, 795, 254-60.

[2] Wang, F.; Xia, L.; Li, X.; Yang, W.; Zhao, Y.; Mao, J. Nano-Ferric Oxide Embedded in Graphene Oxide: High-Performance Electrocatalyst for Nitrogen Reduction at Ambient Condition. *Energ, Envionmental Mater.* **2021**, 4, 88-94.