Supplementary Information

Enhanced Electrochemical Performance in Aluminum Doped δ-MnO₂ Supercapacitor Cathode: Experimental and Theoretical Investigations

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Experimental Methods

Material synthesis

 δ -Al_{0.06}MnO₂ nanosheets/nickel foam electrode was synthesized by hydrothermal method. Firstly, 0.15 g KMnO₄ and 0.006 g Al(NO₃)₃·9H₂O were dissolved in 80 mL deionized water with vigorous stirring for 30 min. Then, a clean nickel foam substrate was immersed into the well stirred solutions. Subsequently, the prepared mixtures were transferred into an autoclave, which were kept at 180 °C for 20 h. Finally, δ - Al_{0.06}MnO₂/Ni-foam was picked out. To remove the loosely attached product, ultrasonic rinsing was performed for 6 min. The final product was baked at 60 °C for 12 h in an oven.

Material characterizations

The crystal structure of the prepared powders was characterized by X-ray diffraction (XRD, PANalytical X'pert Powder). The chemical constituents were analyzed by X-ray photoelectron spectrometer (XPS, ESCA Lab MKII) and energy-dispersive X-ray spectroscopy (EDS, JSM-7800F). The morphology was observed under field-emission scanning electron microscopy (FESEM, JSM-7800F) and transmission electron microscopy (TEM, TECNAI120 Philips).

Electrochemical measurement

The mass loading of the prepared electrode is around 2 mg cm⁻². The electrochemical performance of the prepared electrode was conducted with a CHI electrochemical workstation (Model CHI 660D), using Pt foil and Ag/AgCl as counter and reference electrodes, respectively. Cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) and electrochemical impedance spectroscopy (EIS) tests of the electrodes were performed in different neutral electrolytes. Specific capacitance (C_s) can be calculated from the charge/discharge curves according to:

$$C_S = \frac{2I \int_{t_1}^{t_2} V dt}{m \Delta V^2},\tag{S1}$$

where ΔV is the voltage window, *I* is the discharge current and *m* is the active material mass of the working electrode.

Computational details

The first-principles calculations were performed within the density functional theory framework by using the projector augmented wave (PAW) method, as implemented in the Vienna ab initio simulation package (VASP).^{1, 2} The generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) was used to treat the exchange-correlation interactions.³ The energy and force convergence values were chosen as 10⁻⁵ eV and 0.01 eV Å⁻¹, respectively. The Kohn-Sham orbitals were expanded in plane waves with a cutoff kinetic energy of 500 eV. The Brillouin zone integration and *k*-point sampling were performed with Monkhorst-Pack schemes of $10 \times 10 \times 2$ and $3 \times 3 \times 1$ grid for bulk δ -MnO₂ and surface calculations, respectively.⁴ The GGA+U correlation method was used and the U value of Mn atoms was set as 3.9 eV. The vacuum thickness was set as 15 Å to calculate the surface and adsorption energies. The defect formation energy of different defect samples under neutral condition are calculated by the following formulas:

Vacancy:
$$E_f = E_{v_i} + E_i + \mu_i - E_{initial},$$
 (S2)

Interstitial site:
$$E_f = E_{I_i} - E_{initial} - E_i - \mu_i$$
, (S3)

Replacement:
$$E_f = E_{ij} + E_j + \mu_j - E_{initial} - E_i - \mu_i.$$
 (S4)

Where E_f , E_i and μ_i are defect formation energy, total energy of the *i* metal and chemical potential of the *i* atom, respectively.

Surface energy was computed based on:

$$E_{surf} = \frac{E_{slab} - nE_{bulk}}{2A}.$$
(S5)

Where E_{slab} is the total energy of the slab model, *n* is the number of manganese dioxide units in the slab, E_{bulk} is the total energy of bulk cell with the same number of units, and *A* is the surface area of the slab.

Adsorption energy of lithium atoms adsorbed on the MnO₂ (001) plane was calculated as:

$$E_{ads} = E_{slab+Li} - E_{slab} - E_{Li},\tag{S6}$$

where E_{ads} , $E_{slab+Li}$, E_{slab} and E_{Li} are adsorption energy, total energy of Li atoms absorbed on slab, total energy of slab and total energy of Li metal.

Structure and Composition Analysis

To determine the amount of doped Al in our as prepared δ -Al-MnO₂ sample, ICP experiments were carried out and the results are presented in Tab.S1. The obtained mass of Al and Mn are 0.005 and 0.08 ug ml⁻¹, respectively, which suggest a small Al : Mn ratio of ~0.06:1. The chemical formula of the prepared δ -Al-MnO₂ samples is approximated as δ -Al_{0.06}MnO₂ throughout this article.

The morphology and microstructure of the prepared samples were examined by field electron scanning electron microscopy (FESEM) and transmission electron microscopy (TEM), as displayed in Fig. S1(a, b) and S1(c, d), respectively. For comparison, the morphology of δ -MnO₂ is exhibited in Fig. S2(a, b). It is found that both δ -Al_{0.06}MnO₂ and δ -MnO₂ are nanosheets-like, while the typical thickness of the former is smaller than that of the later. The TEM images in Fig. S1(c, d) demonstrate the interlayer spacing is 0.714 nm, which matches well with the (003) plane of layered δ -MnO₂. The

energy dispersive X-ray spectroscopy (EDS) elemental mapping is displayed in Fig. S1(e), which indicates that K, Mn, O, and Al elements are distributed homogeneously. The atomic percentage of O, Al, K, and Mn is 80.27%, 1.73%, 2.96%, and 15.04% (Fig. S1(f)), respectively. This gives a Al : Mn ration of ~0.1, which agrees qualitatively with that obtained by ICP considering the larger uncertainties of EDS experiments. The extra O is possibly coming from water in the embedded layer. The X-ray diffraction (XRD) results of δ -Al_{0.06}MnO₂ and δ -MnO₂ are shown in Fig. S1(g). All the peaks can be well indexed to the δ -MnO₂(JCPDS. 52-0556) without detectable impurities. Compared with δ -MnO₂, the (003) diffraction peak clearly shifts towards lower values by ~0.3° in δ -Al_{0.06}MnO₂, which is very likely a consequence of enhanced interlayer spacing introduced by Al doping. Note that the (003) peak is also less shaper in δ -Al_{0.06}MnO₂ due to smaller crystal sizes compared with that of δ -MnO₂ [see Fig. S1(a,b) and Fig. S2 (a,b)]⁵.

The X-ray photoelectron spectroscopy (XPS) was also used to investigate the valence states and stoichiometry of δ -Al_{0.06}MnO₂ samples. Fig. S3(a, d) present the XPS spectra of the Survey, Al 2p, Mn 2p, and O 1s orbit, respectively. All the elements can be found in Fig. S3(a). A characteristic peak corresponding to Al³⁺ can be observed at 73.6 eV, as shown in Fig. S3(b). As presented in Fig. S3(c), a typical double-peak structure is observed for Mn, which can be attributed to 2p_{1/2} and 2p_{3/2}, respectively. The 2p_{1/2} peak can be decomposed into three contributions centered at 642.8, 653.8 and 655 eV, which can be attributed to Mn²⁺, Mn³⁺ and Mn⁴⁺, respectively. Similarly, the 2p_{3/2} peak can be assigned to Mn²⁺, Mn³⁺ and Mn⁴⁺, which are locating at 641, 642.2 and 643.6 eV, respectively. Fig. S3(d) exhibits XPS spectra of O 1s, which captures all oxygen including oxygen embedded in the lattice, adsorbed oxygen and oxygen vacancy states.

References

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Tab. S1. ICP results of Al and Mn elements of the as prepared δ -Al-MnO₂ samples.

Element	Al	Mn
Unit (ug ml ⁻¹)	0.005	0.080



Fig. S1. (a-b) SEM images of the as prepared δ -Al-MnO₂, (c-d) TEM images of δ -Al-MnO₂, (e) Elemental mapping of δ -Al-MnO₂, (f) EDS elemental mapping of δ -Al-MnO₂, (g) XRD patterns of δ -Al-MnO₂ and δ -MnO₂.



Fig. S2. (a-b) SEM images of the as prepared δ -MnO₂, (c-d) SEM images of δ -Al_{0.06}MnO₂.



Fig. S3. XPS spectrum of δ -Al_{0.06}MnO₂. (a-d) are Survey, Al 2p, Mn 2p, and O 1s XPS spectrum of δ -Al_{0.06}MnO₂, respectively.



Fig. S4. (a-b) CV and GCD curves of δ -Al_{0.06}MnO₂, (c-d) CV and GCD curves of δ -MnO₂.



Fig. S5. Calculated Peukert's constant k based on specific capacitance obtained from experimental results shown in Fig. S4.



Fig. S6. Optimized crystal structures of δ -Al_{0.06}MnO₂. (a-b) Al atoms adsorbed on two interstitial sites (Al-I₁: AlO₆ octahedron, Al-I₂: AlO₄ tetrahedron), (c) Replacement of an Mn atom by an Al atom (Al-R-Mn), and (d) Replacement of an O atom by an Al atom (Al-R-O).



Fig. S7. (a) Crystal structures of Li atoms adsorbed on δ -Al_{0.06}MnO₂ (001) surface. (b) Crystal structures of Li atoms adsorbed on δ -MnO₂ (001) surface. Here, purple, red, green and blue balls are Mn, O, Li and Al atoms, respectively.



Fig. S8. (a-b) Barrier energy and diffusion path of lithium ion diffused in δ -Al_{0.06}MnO₂ (001) surface. (c-d) Barrier energy and diffusion path of lithium ion diffused in δ -MnO₂ (001) surface.



Fig. S9. (a-b) Differential charge density of δ -Al_{0.06}MnO₂-001 and δ -MnO₂-001, and iso-surface value

is set 0.001