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New insights into the Li-storage mechanism in $\alpha\mbox{-}Ga_2O_3$ anode and the optimized electrode design



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HIGHLIGHTS

- New insights into Li-storage mechanism of α -Ga₂O₃.
- Electrochemical performance optimization via dual carbon decoration.
- Electrochemical reconstruction promoted capacitive contribution for Listorage.

GRAPHICALABSTRACT



ARTICLE INFO

Keywords: Gallium oxide Lithium ion storage mechanism Conversion process Alloying/dealloying Anode

ABSTRACT

Fundamental insights into Li storage mechanism in α -Ga₂O₃ allow manipulating materials with improved electrochemical performance. Here, conversion reactions coupled with alloying/dealloying process are uncovered for Li storage in α -Ga₂O₃ anode, on the basis of *ex-situ* XRD, XPS, SAED and EDS mapping results. Specifically, both processes are part of irreversible. α -Ga₂O₃ decorated with amorphous carbon and graphene (α -Ga₂O₃@C@G) and nitrogen doping are successfully fabricated via a facile approach, showing distinctly improved performance compared with pristine α -Ga₂O₃ and α -Ga₂O₃ decorated with graphene (α -Ga₂O₃@G). In the Ga₂O₃@C@G, dual carbon improves the electronic conductivity and facilitates electrochemical reconstruction of the Ga₂O₃@C@G upon cycling that renders high lithium ion diffusion, giving rise to enhanced capacitive contribution for lithium storage. As a result, the Ga₂O₃@C@G exhibits high discharge/charge capacity of 458/447.3 mAh g⁻¹ after 50 cycles at 0.1 A g⁻¹, with capacitive contribution of 59.2% for lithium ion storage at a scan rate of 1 mV s⁻¹.

1. Introduction

Lithium ion batteries (LIBs) have proven highly efficient energy

storage devices for power source dominating the portable electrics market, as well as promising power supply for the coming electric vehicles and smart grid storage systems [1–3]. However, the energy

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density and safety performance still need to be improved to keep pace with ever-growing demand of energy storage needs. To achieve this goal, searching advanced materials with higher specific capacity and appropriate working potential are highly anticipated [4–10].

III-group elements have long been in the spotlight of both fundamental research and practical application owing to their fascinating chemicophysical properties. They are widely used for doping element inII-VI group semiconductors to tuning the electric, optical, thermoelectric properties [11-14], and also being indispensable element for constructing IV-Vgroup semiconductors [15-21]. As a typical III-group element, Ga based compounds such as GaN, GaAs, GaTe, GaS and GaP are intensively studied as light-emitting diode, semiconductor laser, thin film solar cell, transparent thin film transistor and gas detector owing to their prominent optical and electric properties [22-26]. Recently, GaN and Ga₂O₃ are proven as potential photocatalyst, coating layer for cathode material of LIBs, and anode material for supercapacitors and LIBs [8,27–31]. For instance, Ni et al. designed a freestanding electrode with core-shell architecture of amorphous GaN depositing on Cu nanorod, with electric but electrochemical inert Cu core improving the electronic conductivity and structure stability of the electrode in cycling [8]. Based on *ex-situ* XPS, EDS mapping and SAED analysis, a possible conversion mechanism is proposed for Li storage in GaN. Patel et al. fabricated α , β and γ -phase Ga₂O₃, and they found α -Ga₂O₃ exhibits the best cycle stability (263 mAh g^{-1} after 40 cycles), and mixed phase $(\alpha+\beta+\gamma)$ Ga₂O₃ hybridizing with reduced graphene oxide (rGO) is viable to improve the performance [32]. According to CV curves, partially irreversible conversion and reversible alloying/dealloying mechanism are proposed for Li storage in α-Ga₂O₃. Nevertheless, main challenges of GaN and Ga₂O₃ as anode material for LIBs are still there: 1) unclear Li storage mechanism (i.e, conversion reaction vs. conversion coupled with alloying/dealloying process). 2) the low electronic conductivity (wide bandgap semiconductor) hinders reaction kinetics, resulting in large polarization upon lithiation/delithiation; 3) inevitable volume variation upon cycling, giving rise to unsatisfactory cycleability. Further study to exactly clarify Li⁺ storage mechanism and factors affecting Li storage kinetics are still highly anticipated.

Here, using XPS, SAED and EDS mapping in combination with *ex-situ* XRD, we demonstrate conversion reactions coupled with alloying/ dealloying mechanisms for Li storage in α -Ga₂O₃. Specifically, both of them are part of irreversible. Moreover, doping with N and hybridizing with dual C are proven effective to improve the electrochemical performance of α -Ga₂O₃.

2. Experimental section

2.1. Fabrication

The chemicals are analytical grade and purchased from Sigma-Aldrich. To fabricate α -Ga₂O₃, 2 mmol Ga(NO₃)₃·xH₂O (meta 99.9%) and 5 mmol hexamethylenetetramine (Analytical grade) were dissolved in 40 ml distilled water. After stirring for 20 min, The uniform transparent solution was transferred to a 50 ml teflonlined autoclave and reacted at 120 °C for 24 h. The precipitates were dried and sintered at 400 °C for 10 h in N₂ to obtain α -Ga₂O₃, α -Ga₂O₃@G and α -Ga₂O₃@C@G were fabricated under the same hydrothermal and sintering process, with extra graphite oxide (GO) and GO-glucose additives. GO was synthesized via a modified Hummer's method [33], distilled water was replaced by GO suspension (0.6 mg/ml) to fabricate α -Ga₂O₃@G, and extra 0.02 g glucose was added to fabricate α -Ga₂O₃@C@G. Besides, to obtain homogeneous α -Ga₂O₃@G and α -Ga₂O₃@C@G, the precipitates were collected via freeze drying.

2.2. Material characterization

The composition of the products were characterized by X-Ray powder diffraction (Rigaku Ultima IV, Cu K α radiation, $\lambda = 1.5406$ Å), Micro-Raman spectrometer (Jobin Yvon LabRAM HR800 UV, YGA 532 nm), and XPS spectrometer (Escalab MKII) with Mg K α (h ν = 1253.6 eV) exciting source at a pressure of 1.0×10^{-4} Pa and a resolution of 1.00 eV. The morphology and microstructure of the products were characterized via field-emission scanning electron microscopy (FE-SEM JSM 7500F, JEOL) and transmission electron microscopy (FE, Tecnai G2 F30) equipped with selected area electron diffraction (SAED). To characterize the cycled α -Ga₂O₃@C@G, the cell was disassembled in glove box (MIKROUNA, Super 1220/750, H₂O < 1.0 ppm, O₂ < 1.0 ppm) and washed by dimethyl carbonate before testing.

2.3. Electrochemical measurement

To prepare electrode, active material, acetylene black, and polyvinylidene fluoride (PVDF) with weight ratio of 8:1:1 were coated on copper foil and cut into disc with diameter of 14 mm. 2025 coin-type half cells were assembled in an argon-filled glove box (H₂O < 1.0 ppm, O₂ < 1.0 ppm). The electrolyte consists of 1 M LiPF₆ dissolved in ethylene carbonate and dimethyl carbonate with volume ratio of 1:1, and the membrance is Celgard 2400 microporous polypropylene. The cells were tested via multichannel battery test system (LAND CT2001A, 0.02–3 V). When calculating the specific capacity of the electrode, the weight of α -Ga₂O₃, rGO and amorphous carbon were considered together. The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were tested via electrochemical workstation (CHI660C).

3. Results and discussion

Typical XRD patterns of the as-prepared samples are shown in Fig. 1a. As seen, the diffraction peaks located at 24.5°, 33.8°, 36.0°, 41.4°, 50.2°, 55.1°, 63.3° and 64.7° can be attributed to the (012), (104), (110), (113), (024), (116), (214) and (300) faces of α -Ga₂O₃, which is in good agreement with JCPDS, no. 06-0503. Hybridizing with graphene and/or graphene/C doesn't change the phase of α-Ga₂O₃, but accompanying the reduce of intensity of diffraction peaks [34]. This variation may be relevant to the coverage of graphene and/or coating amorphous C on the surface of Ga₂O₃. The coverage or coating effect can also be reflected via Raman spectra. As shown in the inset of Fig. 1b, pristine Ga_2O_3 exhibits weak peaks (i.e., 216, 284, 431, 573 and 686 cm⁻¹) owing to low crystallinity. The α -Ga₂O₃ was obtained via annealing GaOOH in 400 °C in N2 atmosphere (XRD and TG/DSC of GaOOH see Figure s1), while increasing annealing temperature to 600 °C doesn't change the phase of the α -Ga₂O₃ (Raman spectrum see ESI, Figure s2) [35]. After combining with graphene and amorphous C, Raman peaks of Ga₂O₃ become much weaker, accompanying by the appearance of strong peaks of D band (1351 cm^{-1}) and G-band (1586 cm^{-1}) of carbon [36, 37]. TG analysis was used to determine the content of carbon in the α -Ga₂O₃@G and α -Ga₂O₃@C@G. As shown in Fig. 1c, except for the evaporation of absorbed water in the initial heating stage, weight ratio of 14.1% C in α-Ga₂O₃@G and 24.5% C in α-Ga₂O₃@C@G can be approximately estimated. Fig. 1d-f and g-h are SEM images of the α -Ga₂O₃, α -Ga₂O₃@G and α -Ga₂O₃@C@G. As seen, the α -Ga₂O₃ exhibits cuboid-like morphology with mean width, height and length of 400 nm, 400 nm and 1.2 µm, respectively. Hybridization with graphene and/or graphene/C doesn't change the morphology of the α-Ga₂O₃, but the mean width and height reduces slightly to 300 nm. Notably, graphene nanoflakes and α -Ga₂O₃ cuboids are clearly seen (Fig. 1e and h), while α -Ga₂O₃ shows little aggregation. In contrast, graphene and α -Ga₂O₃ shows even distribution in the α -Ga₂O₃@C@G, with a specific architecture of α -Ga₂O₃ encapsulated in graphene and amorphous C. Such morphology variation coincides with the XRD patterns and Raman spectra variation from α -Ga₂O₃ to α -Ga₂O₃@G and α -Ga₂O₃@C@G.

The composition of the α -Ga₂O₃@C@G was further studied via XPS. As shown in Fig. 2a, the survey spectrum clearly confirms the presence of Ga, O, C and N. High resolution spectra of Ga 3d and 2p in Fig. 2b–c



Fig. 1. XRD patterns (a), Raman spectra (b) and TGA curves (c) of the obtained products. Low (d)–(f) and high (g)–(h) magnification SEM images of α -Ga₂O₃, α -Ga₂O₃@G and α -Ga₂O₃@C@G. (d), (g) for α -Ga₂O₃; (e), (h) for α -Ga₂O₃@G; (f), (i) for α -Ga₂O₃@C@G.

exhibit signals of Ga spin-orbit levels. A strong peak at 21.1 eV corresponds to Ga-O bond in Ga₂O₃ [38,39], while a weak peak at 19.7 eV suggests N doping in the crystal structure of Ga₂O₃ [8,40]. Besides, O 2s peak at 23.6 eV may originate from escape of oxygen atoms from Ga₂O₃ during Ar^+ bombardment [41,42]. The presence of Ga_2O_3 can also be confirmed via spin-orbit levels of Ga $2p_{3/2}$ and Ga $2p_{1/2}$ of Ga³⁺, locating at 1118 and 1145 eV, respectively [43,44]. O 1s spectrum in Fig. 2d exhibits two peaks at 531.8 and 532.8 eV, corresponding to O-Ga bond and C-O/OH⁻ adsorption, respectively [45,46]. C 1s spectrum (Fig. 2e) can be fitted by four peaks centred at 284.7, 285.3, 286.2 and 289.6 eV, coinciding with the binding energies of graphite C (sp²), C=N, C-N and C-O bonds, respectively [36,47,48]. N1s spectrum (Fig. 2f) can be divided into five peaks, in which the peaks at 398.5 and 399.9 eV correspond to pyridine and pyrrolic N, and the peaks near 395.6 eV, 397.2 eV and 399.1 eV correspond to C-N, Ga-N and C=N chemical bonds [8,47,49].

The microstructure of the α -Ga₂O₃@C@G was further studied via TEM and HRTEM. TEM images in Fig. 2g and h indicate homogeneous hybridization between α -Ga₂O₃ and graphene in the α -Ga₂O₃@C@G. The clear diffraction spots in Fig. 2i corroborate the α -Ga₂O₃ are well crystallized. Moreover, amorphous C and graphene can be well distinguished (Fig. 2j). The lattice fringes of α -Ga₂O₃ is unclear probably results from the surface coating of amorphous C and/or N doping [45]. The microstructure of the α -Ga₂O₃@C@G is studied via EDS mapping.

As shown in Fig. 2k, clear rod-like distribution of Ga and O corresponds to Ga_2O_3 , while the symmetric distribution of C and N indicates homogeneous hybridization between Ga_2O_3 and graphene as well as even N doping in the $Ga_2O_3@C@G$. Note the rod-like profile in C distribution stems from coating amorphous carbon on the surface of Ga_2O_3 .

The initial three charge/discharge profiles of the α-Ga₂O₃@C@G are shown in Fig. 3a. From which continuous sloping potential regions (0.65-0.02 V for the first cathodic scan, 1.2-0.02 V for the subsequent cathodic scan, 0.02-2.5 V for all anodic scan) can be identified, suggesting successive electrochemical reactions upon lithiation/delithiation. The α -Ga₂O₃@C@G delivers initial discharge/charge capacities of 975.4/669.9 mAh g⁻¹ at 0.2 A g⁻¹. When increasing specific current to $0.5\,\mathrm{A\,g^{-1}}$, the discharge/charge capacities maintain of 343.5/ 334.9 mAh g $^{-1}$ after 50 cycles (Fig. 3b). CV curves of the α -Ga_2O_3@C@G (Fig. 3c) shows typical characteristics of conversion anode material such as Fe₃O₄, CoO, NiO, CuO, Ni₃S₂ and NiS (i.e., obvious difference between the initial and subsequent cathodic curve and close profile for all anodic curves) [50-55]. Two continuous reduction peak centered at 0.36 and 0.05 V correspond to the formation of solid electrolyte film (SEI), the reduction of Ga_2O_3 to Ga and further formation of Li_2Ga [31, 56–58]. Notably, the reduction peaks shift to high potential region in the subsequent cycles owing to the activation of the electrode [9,59-61]. In the anodic scan, two oxidation peaks centered at 0.35 and 0.98 V can ascribe to the release of lithium ion coupled with dealloying process and



Fig. 2. (a)–(f) XPS spectra of the sample α -Ga₂O₃@C@G. (a) Survey spectrum; High resolution spectrum of (b) Ga 3d, (c) Ga 2p, (d) O 1s, (e) C 1s and (f) N 1s; (g)–(k) microstructure information of the α -Ga₂O₃@C@G. (g) low and (h) High magnification TEM image; (i) SAED pattern; (j) HRTEM image; (k) EDS mapping for Ga, O, C and N.

subsequent oxidation of Ga [31,56,58]. G and C facilitate the reaction kinetics of Ga₂O₃ upon lithiation/delithiation (CV curves of Ga₂O₃ and Ga₂O₃@G see ESI, Figure s3), improving the cycleability. As shown in Fig. 3d, the α -Ga₂O₃@C@G electrode exhibits discharge/charge capacities of 350.1/338.6 mAh g⁻¹ at 0.15 A g⁻¹ after 50 cycles, higher than that of α -Ga₂O₃@G (159.6/152.9 mAh g⁻¹) and α -Ga₂O₃ (105.3/105 mAh g⁻¹). Meanwhile, the specific capacity of the α -Ga₂O₃@C@G increases along with the decreasing of specific current (i.e., 458/447.3 mAh g⁻¹ after 50 cycles at 0.1 A g⁻¹, see ESI, Figure s4).

Reaction kinetics of the α -Ga₂O₃@C@G electrode are studied to understand the performance improvement. According to equation of *i* $(V) = k_1v + k_2v^{1/2}$, the capacitive-contributed charge storage can be extracted by separating the k_1v part, where k_1v is constant and can be deduced from CV curves at different scan rates (Fig. 3e–f) [10,62–64]. These values increase from 41.5% to 59.2% along with the increase of scan rate from 0.2 to 1.0 mV s⁻¹ (Fig. 3g). The capacitive contribution of the α -Ga₂O₃@C@G is distinctly improved compared with that of α -Ga₂O₃@G and α -Ga₂O₃ (see ESI, Figure s5). Notably, capacitive contribution for lithium ion storage of the α -Ga₂O₃@C@G gradually enhances upon cycling, reaching 60.6% and 66.4% after 10 and 20 cycles, respectively (see ESI, Figure s6).

The kinetics variation of the α -Ga₂O₃@C@G electrode upon cycling correlates intimately with the morphology variation. As shown in Fig. 4a–d, cuboid-like morphology of α -Ga₂O₃ is partially preserved after 10 and 20 cycles, while vague profiles of these cuboids imply structure destruction upon lithiation/delithiation. The cuboid-like morphology totally vanishes after 50 cycles, evolving into homogeneous particles with mean size of several hundred nanometers (see ESI, Figure s7). This



Fig. 3. Electrochemical performance of the α -Ga₂O₃@C@G electrode. (a) The initial there charge/discharge curves and (b) Cycle performance at specific current of 0.2–0.5 A g⁻¹; (c) Cyclic voltammogram curves at a scan rate of 0.2 mV s⁻¹; (d) Capacity retention at specific current of 0.15 A g⁻¹; (e) Cyclic voltammogram curves at different scan rate; (f) Capacitive contribution diagram at scan rate of 1 mV s⁻¹; (g) Capacitive contribution at different scan rates.

is similar to coordinated electrochemical reconstruction of NiV₃O₈/ graphite upon cycling. The NiV₃O₈ nanoplates evolve into smaller particles coating solidly on the surface of graphite [65], giving rise to enhanced electric conductivity. Here the electronic conductivity of the α -Ga₂O₃ can be distinctly improved via hybridizing with graphene and amorphous C (Fig. 4f), and gradually enhanced via coordinated electrochemical reconstruction upon cycling (Fig. 4f). Meanwhile, according to Warburg factor (the inset in Fig. 4e and f), it is found that the α -Ga₂O₃@C@G exhibits improved lithium ion diffusion than α -Ga₂O₃ and α -Ga₂O₃@G, and the lithium ion diffusion gradually enhanced upon cycling. The enhanced electronic conductivity and lithium ion diffusion facilitate fast reaction kinetics, inducing improved capacitive contribution for lithium storage [10,63].

To gain more insights into the lithium ion storage mechanism in α -Ga₂O₃, ex-situ XRD characterizations were carried out under different state of charge (SOC). As shown in Fig. 5a and b, all discharge and charge curves are well overlapped in the same voltage region, suggesting steady lithiation/delithiation process of α -Ga₂O₃. According to these charge/discharge curves, phase conversion of α -Ga₂O₃ upon lithiation/ delithiation is studied. Ex-situ X-ray diffraction of the α -Ga₂O₃ is shown in Fig. 5c. As seen, new diffraction peaks near 21.39°, 31.36° and 32.26° appear when discharging to 0.36 V, which can be indexed as Li₂Ga [56]. These diffraction peaks further increase when discharging to 0.02 V. Meanwhile, diffraction peaks near 33.8° and 36.0°, corresponding to (104) and (110) faces of α -Ga₂O₃, gradually disappear upon discharging. Note that Li₂Ga appears (0.36 V) with lithium ion uptake <6, implying alloying process occurs at the expense of conversion reactions (i.e.,

uptake of 6 lithium ions). Meanwhile, total uptake of lithium ions >8 suggests extra Li⁺ consumption stemming from the formation of SEI. Electrochemical reactions upon discharging can be described as [56, 66–69]:

$$Ga_2O_3 + 6Li^+ + 2e^- \rightarrow Ga + Li_2O \tag{1}$$

$$Ga + 2Li^+ + 2e^- \rightarrow Li_2Ga \tag{2}$$

Upon charging, the diffraction peaks of Li₂Ga remain up to 1.0 V with lithium ion release >3, implying inadequate dealloying process upon delithiation. When charging to 3.0 V, all diffraction peaks vanish, suggesting amorphization. This makes difficult to determine detailed phase of delithiated products. However, based on charge capacity of the α -Ga₂O₃ (<7 lithium ions release), it can be confirmed that α -Ga₂O₃ is not fully reverted upon delithiation. Possible electrochemical reactions are:

$$Li_2Ga \rightarrow Ga + 2e^- + 2Li^+$$
(3)

$$xGa + yLi_2O \rightarrow Ga_xO_y + 2yLi^+ + 2ye^-$$
(4)

This postulation is further supported by TEM, SAED and EDS mapping results. As shown in low magnification TEM images in Fig. 6a, the lithiated $(0.02 \text{ V}) \alpha$ -Ga₂O₃ exhibits general cuboid-like morphology with coarse surface, surrounded by numerous nonosized particles. High magnification TEM image (Fig. 6b) indicates the coarse morphology is composed of hierarchical nanoparticles, implying morphology evolution of Ga₂O₃ upon lithiation. Such morphology is similar to that of lithiated NiO, CoO and FeO, in which Co, Ni and Fe is surrounded by amorphous



Fig. 4. Low (a), (b) and high (c), (d) magnification SEM images of α -Ga₂O₃@C@G electrode after 10 and 20 cycles. (a), (c) for 10 cycles, (b), (d) for 20 cycles; (e), (f) EIS spectra for fresh α -Ga₂O₃@G and α -Ga₂O₃@C@G electrodes and α -Ga₂O₃@C@G electrode after 10 and 20 cycles. The inset in (e), (f) is the fitted values of Rct and Nyquist plots of the real part of complex impedance vs. ω^{-1} .

Li₂O matrix [70]. Moreover, amorphous Li₂O, Ga and Li₂Ga in the lithiated products are confirmed via SAED pattern (inset in Fig. 6b), suggesting insufficient electrochemical reactions (2) upon lithiation. EDS mapping (Fig. 6c–f) reveals that O shows much wider distribution than Ga, implying the reduction Ga_2O_3 and the formation of other oxide upon lithiation (i.e., Li₂O). Notably, N shows weak signal with similar distribution to O, which may be relevant to partial formation of nitride (i.e., Li₃N) owing to the reduction of GaN [8].

The evolution of Ga valence state sheds more light on the phase transformation of α -Ga₂O₃ upon lithiation/delithiation. As shown in survey spectrum in Fig. 7a, relative intensity of O 1s signal changes obviously upon lithiation and delithiation, implying different chemical bonding environment. For the fully lithiated α -Ga₂O₃ (Fig. 7b), a broad peak centered at 20.2 eV can be ascribed to Ga 3d spin orbit for Ga^{x+} (x = 1–3), and a weak peak near 18.4 eV coincides with Ga [71–74]. The reduction of Ga^{x+} (i.e., from Ga³⁺ to Ga⁰) will lead to increase in peak intensity of O 2s signal at 23.5 eV [72]. After delithiation, signals of O 2s and Ga are observed, with weakened intensity owing to the reversible oxidation. A broad peak near 19.8 eV corresponds to Ga^{x+} (x = 1, 2) [71, 73]. Note that the valence state of Ga in the lithiated Ga₂O₃ is higher than that of delithiated Ga₂O₃, which may be relevant to inevitable

oxidation of highly active Li₂Ga alloy in air. Contrastively, three peaks at 531.6, 531.8 and 532.8 eV for O 1s spectrum (Fig. 7c) correspond to Ga_xO (x = 2–2/3), CO₃^{2–} and OH[–] adsorption [71,75], where CO₃^{2–} may stem from the conversion from Li₂O to Li₂CO₃ during exposing in air [75]. Except weak peak (532.8 eV) for OH[–] adsorption, O 1s spectrum for the delithiated Ga₂O₃ (531.2 eV) coincides with Ga–O bond in Ga_xO (x = 1, 2). Ga and O spectrum for the fully lithiated/delithiated α -Ga₂O₃ further prove irreversible conversion process upon lithiation/delithiation. Based on above discussion, conversion reactions coupled with alloying/dealloying mechanisms (equations (1)–(4)) of α -Ga₂O₃ upon lithiation/delithiation can be confirmed, with partial irreversibility for both conversion and alloying/dealloying reactions.

4. Conclusions

 α -Ga₂O₃ as anode for lithium ion batteries are systematically studied in terms of fabrication, lithium storage mechanism and performance optimization. A facile hydrothermal pretreatment followed by low temperature sintering are developed to prepare N doped α -Ga₂O₃@C@G composite. N doping and graphene and amorphous C hybridization are proven effective to improve the performance of α -Ga₂O₃, owing to



Fig. 5. Discharge/charge curves and XRD patterns of α -Ga₂O₃ under different state. (a) discharging to 0.36 and 0.02 V; (b) charging to 0.36, 1.0 and 3.0 V; (c) XRD patterns.



Fig. 6. Low (a) and high (b) magnification TEM image, and (d)-(f) element mapping for fully lithiated α-Ga₂O₃. The inset in (a) is corresponding SAED pattern.

improved electronic conductivity and facilitated electrochemical reconstruction inducing high lithium ion diffusion. Conversion reactions coupled with alloying/dealloying mechanisms are confirmed for the lithium ion storage of α -Ga₂O₃, during which both processes exhibit

partial irreversibility. As the electrochemical irreversibility upon lithiation/delithiation correlates ultimately with the reaction kinetics of α -Ga_2O_3 (i.e., electronic conductivity and lithium ion diffusion), further optimizing these properties may be promising to significantly improve



Fig. 7. XPS spectra of α-Ga₂O₃ at fully lithiated and delithiated state. (a) For survey spectrum; High resolution spectrum of (b) Ga 3d and (c) O 1s.

the performance of α -Ga₂O₃. Nevertheless, great potential of Ga₂O₃ as anode for LIBs has been demonstrated via these important findings in this work.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jpowsour.2019.05.087.

References

- [1] D. Larcher, J.M. Tarascon, Nat. Chem. 7 (2015) 19–29.
- [2] S.Y. Lee, K.H. Choi, W.S. Choi, Y.H. Kwon, H.R. Jung, H.C. Shin, J.Y. Kim, Energy Environ. Sci. 6 (2013) 2414.
- [3] N. Nitta, F. Wu, J.T. Lee, G. Yushin, Mater. Today 18 (2015) 252-264.
- [4] Z. Wang, L. Zhou, X.W. David Lou, Adv. Mater. 24 (2012) 1903–1911.
- [5] Y. Wang, G. Cao, Adv. Mater. 20 (2008) 2251–2269.
- [6] Y. Sun, N. Liu, Y. Cui, Nat. Energy 1 (2016) 16071.
- [7] T. Kennedy, M. Brandon, K.M. Ryan, Adv. Mater. 28 (2016) 5696–5704.
 [8] S. Ni, P. Huang, D. Chao, G. Yuan, L. Zhang, F. Zhao, J. Li, Adv. Funct. Mater. 27
- (c) 5. M, F. Huang, D. Chao, G. Tuan, L. Zhang, F. Zhao, J. Li, Auv. Funct. Water. 27 (2017) 1701808.
- [9] S. Ni, X. Lv, J. Ma, X. Yang, L. Zhang, J. Power Sources 248 (2014) 122–129.
- [10] S. Ni, J. Ma, X. Lv, X. Yang, L. Zhang, J. Mater. Chem. A 2 (2014) 20506–20509.
 [11] W.J. Park, H.S. Shin, B.D. Ahn, G.H. Kim, S.M. Lee, K.H. Kim, H.J. Kim, Appl. Phys. Lett. 93 (2018), 083508.
- [12] O. Nakagawara, Y. Kishimoto, H. Seto, Y. Koshido, Y. Yoshino, T. Makino, Appl. Phys. Lett. 89 (2016), 091904.
- [13] H.J. Ko, Y.F. Chen, S.K. Hong, H. Wenisch, T. Yao, D.C. Look, Appl. Phys. Lett. 77 (2000) 3761–3763.
- [14] Z.F. Zhou, G.K. Ren, X. Tan, R. Liu, C. Liu, Y.H. Lin, C.W. Nan, J. Mater. Chem. A 6 (2018) 24128–24135.
- [15] X. Sun, Y. Li, Angew. Chem. 116 (2014) 3915-3919.
- [16] K. Sasaki, A. Kuramata, T. Masui, E.G. Víllora, K. Shimamura, S. Yamakoshi, Appl. Phys. Express 5 (2012), 035502.
- [17] S. Nakamura, Y. Harada, M. Seno, Appl. Phys. Lett. 58 (1991) 2021–2023.
- [18] Y. Tian, J. Yan, Y. Zhang, Y. Zhang, X. Chen, Y. Guo, J. Wang, J. Li, Nanoscale 8 (2016) 11012–11018.
- [19] C.Y. Chen, G. Zhu, Y. Hu, J.W. Yu, J. Song, K.Y. Cheng, L.H. Peng, L.J. Chou, Z. L. Wang, ACS Nano 6 (2012) 5687–5692.
 [20] P. Saad, C. Fager, H. Cao, H. Zirath, K. ersson, T. IEEE, Microw. Theory 58 (2010)
- 1677-1685.
- [21] Y. Arakawa, K. Ueno, H. Imabeppu, A. Kobayashi, J. Ohta, H. Fujioka, Appl. Phys. Lett. 110 (2017), 042103.
- [22] T.R. Kuykendall, A.M. Schwartzberg, S. Aloni, Adv. Mater. 27 (2015) 5805–5812.
 [23] S. Hu, C.Y. Chi, K.T. Fountaine, M. Yao, H.A. Atwater, P.D. Dapkus, N.S. Lewis, C. Zhou, Energy Environ. Sci. 6 (2013) 1879.

- [24] S. Huang, Y. Tatsumi, X. Ling, H. Guo, Z. Wang, G. Watson, A.A. Puretzky, D. B. Geohegan, J. Kong, J. Li, T. Yang, R. Saito, M.S. Dresselhaus, ACS Nano 10 (2016) 8964–8972.
- [25] P. Hu, L. Wang, M. Yoon, J. Zhang, W. Feng, X. Wang, Z. Wen, J.C. Idrobo, Y. Miyamoto, D.B. Geohegan, K. Xiao, Nano Lett. 13 (2013) 1649–1654.
- [26] J. Greil, S. Assali, Y. Isono, A. Belabbes, F. Bechstedt, F.O. Valega Mackenzie, A. Y. Silov, E.P. Bakkers, J.E. Haverkort, Nano Lett. 16 (2016) 3703–3709.
- [27] Y. Hou, X. Wang, L. Wu, Z. Ding, X. Fu, Environ. Sci. Technol. 40 (2006) 5799–5803.
- [28] S. Jin, X. Wang, X. Wang, M. Ju, S. Shen, W. Liang, Y. Zhao, Z. Feng, H.Y. Playford, R.I. Walton, C. Li, J. Phys. Chem. C 119 (2015) 18221–18228.
- [29] M.R. Laskar, D.H. Jackson, Y. Guan, S. Xu, S. Fang, M. Dreibelbis, M. K. Mahanthappa, D. Morgan, R.J. Hamers, T.F. Kuech, ACS Appl. Mater. Interfaces 8 (2016) 10572–10580
- [30] S. Wang, L. Zhang, C. Sun, Y. Shao, Y. Wu, J. Lv, X. Hao, Adv. Mater. 28 (2016) 3768–3776.
- [31] X. Tang, X. Huang, Y. Huang, Y. Gou, J. Pastore, Y. Yang, Y. Xiong, J. Qian, J. D. Brock, J. Lu, L. Xiao, H.D. Abruna, L. Zhuang, ACS Appl. Mater. Interfaces 10 (2018) 5519–5526.
- [32] S.B. Patil, I.Y. Kim, J.L. Gunjakar, S.M. Oh, T. Eom, H. Kim, S.J. Hwang, ACS Appl. Mater. Interfaces 7 (2015) 18679–18688.
- [33] W.S. Hummers Jr., R.E. Offeman, J. Am. Chem. Soc. 80 (1958), 1339-1339.
- [34] Y. Shi, J.Z. Wang, S.L. Chou, D. Wexler, H.J. Li, K. Ozawa, H.K. Liu, Y.P. Wu, Nano Lett. 13 (2013) 4715–4720.
- [35] D. Machon, P.F. McMillan, B. Xu, J. Dong, Phys. Rev. B 73 (2006), 094125.
- [36] S. Ni, J. Zhang, J. Ma, X. Yang, L. Zhang, J. Power Sources 296 (2015) 377–382.
- [37] Q. Li, Q. Wei, J. Sheng, M. Yan, L. Zhou, W. Luo, R. Sun, L. Mai, Adv. Sci. Lett. 2 (2015), 1500284.
- [38] J.X. Sun, W. Mi, D.S. Zhang, Z.C. Yang, K.L. Zhang, Y.M. Han, Y.J. Yuan, J.S. Zhao, B. Li, Optoelectron. Lett. 13 (2017) 295–298.
- [39] V. Josepovits, O. Krafcsik, G. Kiss, I. Perczel, Sensor. Actuator. B Chem. 48 (1998) 373–375.
- [40] M. Higashiwaki, S. Chowdhury, B.L. Swenson, U.K. Mishra, Appl. Phys. Lett. 97 (2010), 222104.
- [41] V. Kanazirev, G.L. Price, G. Tyuliev, Zeolites 12 (1992) 846–850.
- [42] D. Zatsepin, D. Boukhvalov, A. Zatsepin, Y.A. Kuznetsova, D. Gogova, V.Y. Shur, A. A. Esin, Superlattice. Microst. 120 (2018) 90–100.
- [43] B. Cheng, E.T. Samulski, J. Mater. Chem. 11 (2001) 2901-2902.
- [44] S.C. Vanithakumari, K.K. Nanda, Adv. Mater. 21 (2009) 3581-3584.
- [45] R. Kumar, P.K. Dubey, R.K. Singh, A.R. Vaz, S.A. Moshkalev, RSC Adv. 21 (2016) 17669–17677.
- [46] S. Ni, J. Zhang, J. Ma, X. Yang, L. Zhang, X. Li, H. Zeng, Adv. Mater. Interfaces 3 (2016), 1500340.
- [47] D. Nan, Z.H. Huang, R. Lv, L. Yang, J.G. Wang, W. Shen, Y. Lin, X. Yu, L. Ye, H. Sun, F. Kang, J. Mater. Chem. A 2 (2014) 19678–19684.
- [48] S. Ni, J. Zhang, J. Ma, X. Yang, L. Zhang, J. Mater. Chem. A 3 (2015) 17951–17955.
 [49] D. Yang, A. Velamakanni, G. Bozoklu, S. Park, M. Stoller, R.D. Piner, S. Stankovich,
- I. Jung, D.A. Field, C.A. Ventrice, R.S. Ruoff, Carbon 47 (2009) 145–152. [50] Z. Chen, Y. Zhang, X. Wang, W. Sun, S. Dou, X. Huang, B. Shi, J. Power Sources 363
- (2017) 209–217.
 [51] K. Cao, L. Jiao, Y. Liu, H. Liu, Y. Wang, H. Yuan, Adv. Funct. Mater. 25 (2015) 1082–1089.
- [52] Z. Fan, J. Liang, W. Yu, S. Ding, S. Cheng, G. Yang, Y. Wang, Y. Xi, K. Xi, R. V. Kumar, Nanomater. Energy 16 (2015) 152–162.
- [53] W. Yang, J. Wang, W. Ma, C. Dong, G. Cheng, Z. Zhang, J. Power Sources 333 (2016) 88–98.
- [54] X. Song, X. Li, Z. Bai, B. Yan, D. Li, X. Sun, Nanomater. Energy 26 (2016) 533–540.
 [55] S. Ni, X. Yang, T. Li, J. Mater. Chem. 22 (2012) 2395.
- [56] J. Saint, M. Morcrette, D. Larcher, J.M. Tarascon, Solid State Ionics 176 (2005) 189–197.
- [57] M.V.V.M. Satya Kishore, U.V. Varadaraju, J. Power Sources 156 (2006) 594–597.
 [58] M. Yang, C. Sun, T. Wang, F. Chen, M. Sun, L. Zhang, Y. Shao, Y. Wu, X. Hao, ACS
- [58] M. Yang, C. Sun, T. Wang, F. Chen, M. Sun, L. Zhang, Y. Shao, Y. Wu, X. Hao, AC Appl. Mater. Interfaces 1 (2018) 4708–4715.

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- [59] X. Wang, L. Qiao, X. Sun, X. Li, D. Hu, Q. Zhang, D. He, J. Mater. Chem. A 1 (2013) 4173–4176.
- [60] X. Sun, C. Yan, Y. Chen, W. Si, J. Deng, S. Oswald, L. Liu, O.G. Schmidt, Adv. Energy Mater. 4 (2014), 1300912.
- [61] S. Ni, X. Lv, J. Ma, X. Yang, L. Zhang, J. Power Sources 270 (2014) 564–568.
- [62] J. Liu, J. Wang, C. Xu, H. Jiang, C. Li, L. Zhang, J. Lin, Z.X. Shen, Adv. Sci. 5 (2018), 1700322.
- [63] D. Chao, C. Zhu, P. Yang, X. Xia, J. Liu, J. Wang, X. Fan, S.V. Savilov, J. Lin, H. J. Fan, Z.X. Shen, Nat. Commun. 7 (2016) 12122.
- [64] C. Chen, Y. Wen, X. Hu, X. Ji, M. Yan, L. Mai, P. Hu, B. Shan, Y. Huang, Nat. Commun. 6 (2015) 6929.
- [65] S. Ni, J. Ma, J. Zhang, X. Yang, L. Zhang, Chem. Commun. 51 (2015) 5880–5882.
 [66] C.F. Zhang, S.H. Park, O. Ronan, A. Harvey, A. Seral-Ascaso, Z. Lin, N. McEvoy, C.
- S. Boland, N.C. Berner, G.S. Duesberg, P. Rozier, J.N. Coleman, V. Nicolosi, Small 13 (2017), 1701677.

- [67] J.J. Ding, Y.N. Zhou, Y.H. Cui, Z.W. Fu, ECS Electrochem. Lett. 1 (2012) 7–9.
- [68] Y. Song, Y. Li, L. Zhu, Z. Pan, Y. Jiang, P. Wang, Y.N. Zhou, F. Fang, L. Hu, D. Sun, J. Mater. Chem. A 6 (2018) 1086–1093.
- [69] H. Senoh, H. Kageyama, T. Takeuchi, K. Nakanishi, T. Ohta, H. Sakaebe, M. Yao, T. Sakai, K. Yasuda, J. Power Sources 196 (2011) 5631–5636.
- [70] P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, J.M. Tarascon, Nature 407 (2000) 496–499.
- [71] B.J. Flina, N.S. McIntyre, Surf. Interface Anal. 15 (1990) 19–26.
- [72] B. Zheng, W.M. Hua, Y.H. Yue, Z. Gao, J. Catal. 232 (2005) 143–151.
- [73] A. Petitmangin, B. Gallas, C. Hebert, J. Perrière, L. Binet, P. Barboux, X. Portier, Appl. Surf. Sci. 278 (2013) 153–157.
- [74] Y. Mizokawa, H. Iwasaki, R. Nishitanl, S. Nakamura, J. Electron Spectrosc. 14 (1978) 129–141.
- [75] K.P.C. Yao, D.G. Kwabi, R.A. Quinlan, A.N. Mansour, A. Grimaud, Y.L. Lee, Y.C. Lu, Y.S. Horn, J. Electrochem. Soc. 160 (2013) 824–831.