

## King Saud University

## Arabian Journal of Chemistry

www.ksu.edu.sa



### **ORIGINAL ARTICLE**

# Tunable electronic properties of free-standing Fedoped GaN nanowires as high-capacity anode of lithium-ion batteries



## Kefeng Xie<sup>a,\*</sup>, Jie Wang<sup>a</sup>, Sanchuan Yu<sup>c</sup>, Ping Wang<sup>c</sup>, Changlong Sun<sup>b,\*</sup>

<sup>a</sup> School of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou 730070, Gansu, PR China <sup>b</sup> College of Materials Science and Engineering, Qingdao University of Science and Technology, Qingdao 266042, Shandong, PR China

<sup>°</sup> Ningbo Sanbang Microfiber Co., Ltd, Ningbo 315000, Zhejiang, PR China

Received 17 February 2021; accepted 8 April 2021 Available online 15 April 2021

#### **KEYWORDS**

Fe doping; GaN nanowires; Anode; Lithium-ion batteries; Density functional theory **Abstract** As an electrode in lithium-ion batteries (LIBs), gallium nitride (GaN) suffers from inferior conductivity and unsatisfied capacity performance. Although nanostructure designing and carbon coating strategies have been adopted to address this concern, improved Li<sup>+</sup> storage performance remains highly desirable. In this work, Fe doping strategy was adopted in asprepared GaN via chemical vapor deposition. Fe doping enhanced electrical conductivity and charge-transfer efficiency. Results showed that the covalent doping of Fe into GaN nanowires provided abundant nanochannels and realized efficient ionic transfer and reduced Li<sup>+</sup> diffusion barrier. These Fe covalently doped GaN nanowire arrays exhibited capacities of up to 612.3 mAh g<sup>-1</sup> at 0.1 A g<sup>-1</sup> after 200 cycles and 338.2 mAh g<sup>-1</sup> at 5.0 A g<sup>-1</sup> after 500 cycles. Density functional theory calculations confirmed that the crystal and band structures were tuned to intensively enhance the ionic transfer efficiency and electrical conductivity and enhance the Li<sup>+</sup> storage performance. The electron density strategy provided a significant reference for the rational construction of efficient Li<sup>+</sup> storage electrode and beyond.

© 2021 The Author(s). Published by Elsevier B.V. on behalf of King Saud University. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

#### 1. Introduction

\* Corresponding authors.

E-mail addresses: xiekefeng@mail.lzjtu.cn (K. Xie), happysunchang-long@126.com (C. Sun).

Peer review under responsibility of King Saud University.



As widely used lithium-ion batteries (LIBs) anodes (Yang et al., 2018; Lu et al., 2018; Huang et al., 2015; Huang et al., 2020; Wang et al., 2017); traditional graphite anodes has an insufficient theoretical capacity (372 mAh  $g^{-1}$ ) and inferior, which restrict its further application (Ding et al., 2019; Dou et al., 2019). Owing to their lower conversion potentials (Lai et al., 2014), metal nitrides have been considered as the substi-

https://doi.org/10.1016/j.arabjc.2021.103161

1878-5352 © 2021 The Author(s). Published by Elsevier B.V. on behalf of King Saud University.

This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

tute for graphite anodes (Baggetto et al., 2010; Fu et al., 2004; Sun and Fu, 2012; Xu et al., 2012; Snyder et al., 2007; Pereira et al., 2002; Sun et al., 2020). However, the unsatisfied charging capacity and cycling performance continue to restrict the electrochemical performance of these metal nitride-based anodes (Raman et al., 2014; Han et al., 2018). To solve these problems, various approaches were adopted to enhance the electrochemical performances of these LIB anodes (Li et al., 2018; Li et al., 2020). Morphological control is the most used method, including nanowires, nanofibers, nanosheets, and nanoparticles, but it could not fundamentally solve the poor cycling performance (He et al., 2019; Li et al., 2019; Li et al., 2019; Rodriguez et al., 2020; Santiago et al., 2019; González-Macías et al., 2018: McNulty et al., 1819: Yang et al., 2020: Vishnu et al., 2020). Carbon coating is also a common modification method for improving electrochemical performance (Ali et al., 2017; Balogun et al., 2015; Zhou et al., 2015). However, carbon coating could not promote the intrinsic electrical conductivity of anodes. Thus, developing advanced anode materials with high electrical conductivity and structural stability and abundant active sites are essential for advanced electrochemical performance in the energy storage field (Tang et al., 2019; Zhang et al., 2019).

Gallium nitride (GaN) has been extensively researched as LIB anodes (Zhang et al., 2018; Ni et al., 2017; Peng et al., 2020). It has excellent structure and chemical stability, showing negligible volume change in electrochemical reaction processes. However, the electrochemical performance of intrinsic GaN is still limited by the unsatisfied Li<sup>+</sup> transfer kinetic. For instance, the intrinsic GaN anode capacity is  $189 \text{ mA h g}^{-1}$ at 0.1 A  $g^{-1}$ , which seriously restricts its wide application (Sun et al., 2017). Therefore, morphological control strategies (such as nanowires, nanosheets, and nanofibers) were considered to enhance the Li<sup>+</sup> storage performance of GaN nanostructures (Peng et al., 2020; Sun et al., 2017; Jung et al., 2019; Sun et al., 2018). However; these strategies have no significant effect on the Li<sup>+</sup> storage performance of GaN nanostructures, and the semiconducting characteristic restricts the charge-transfer efficiency of intrinsic GaN nanostructure anodes. Therefore, the ionic transfer efficiency must be improved, and the Li<sup>+</sup> diffusion barrier of GaN anodes must be reduced. Aside from morphological control strategies, foreign atom doping could heighten the conductivity and Li<sup>+</sup> transfer and improve Li<sup>+</sup> storage performance (Zhou et al., 2019; Ma et al., 2020; Wu et al., 2019). Therefore, the Li<sup>+</sup> storage performance of foreign atom-doped GaN could be obviously manipulated by changing the electron densities (Xiang and Wei, 2008). As transition metallic atoms with much free electrons, Fe atoms have been considered as foreign atoms for increasing the free electrons of an anode material. Therefore, Fe atom doping could improve electronic conductivity and charge-transfer efficiency (Wu et al., 2019; Zhou et al., 2019; Liu et al., 2019; Mueller et al., 2015). According to the literature; foreign atom doping (Cu, Fe, and P) could prominently change the intrinsic electronic properties of GaN, indicating the immense potential for enhancing the electrochemical performance of GaN nanostructure anode (Li et al., 2010; Seong et al., 2007). As a metallic element, Fe has much free electrons. The number of free electrons of anode material increases when Fe is incorporated. Therefore, with unfilled 3d orbitals and variable chemical states, Fe is vital in the electronic conductivity and electrochemical performance of the anode materials of LIBs. To the

best knowledge of the authors, Fe-doped GaN (Fe-GaN), as an active anode nanostructure for LIB, has not been reported. Moreover, in the form of nanowire array, Fe-GaN nanowires have appropriate surface area and high permeability, which benefits Li<sup>+</sup> diffusion (Liu et al., 2010; Liu et al., 2012). The direct contact between nanoarray and flexible graphite layer ensures adequate charge transfer during electrochemical reaction (Tan et al., 2018; Wang et al., 2018).

In the present work, intrinsic GaN and Fe-GaN nanowires were prepared via chemical vapor deposition (CVD) and studied as anode materials of LIBs. X-ray photoelectron spectroscopy (XPS) analysis revealed the covalent bonding between Fe and GaN. The self-supported Fe-GaN nanowires arrays could shorten the charge-transfer distance and reduce the Li<sup>+</sup> diffusion energy barrier. Therefore, the impressive electrochemical performance of Fe-GaN nanowire anode primarily resulted from the heterogeneous atom doping and nanostructure designing, and this performance could be further confirmed by density functional theory (DFT) studies. As anode materials of LIBs, Fe-GaN nanowire anode exhibited capacities of up to 612.3 mAh  $g^{-1}$  after 200 cycles at 0.1 A  $g^{-1}$  and 338.2 mAh  $g^{-1}$  after 500 cycles at 5.0 A  $g^{-1}$ . Thus, heterogeneous atom doping has a potential application for high-rate LIBs.

#### 2. Experimental section

#### 2.1. Preparation of Fe-GaN nanowires

Fe-GaN nanowires were prepared via CVD.  $Ga_2O_3$  and  $NH_3$  were used as raw materials, while  $Fe(NO_3)_2$  was used as dopant source. Graphite layer was used as conducting layer to deposit the as-grown Fe-GaN nanowires. The distance between the alumina boat and the graphite layer was 2 in.. Before the furnace was heated to 1100 °C under N<sub>2</sub>, the quartz reactor was dewatered via vacuum pumping. Fe-GaN nanowires were obtained under  $NH_3$  atmosphere at 1100 °C for 15 min. The furnace was then cooled down to room temperature under  $N_2$ .

#### 2.2. Electrochemical measurements

The electrochemical performances of the Fe-GaN nanowire working electrodes were tested in the CR2016 half-cell to avoid oxygen and moisture. The monolithic Fe-GaN nanowires/-graphite layers were tailored (12 mm). On the graphite layer, the loading density was 1.9 mg cm<sup>-2</sup>. The electrolyte was LiPF<sub>6</sub> (1.0 M) in the mixed diethyl carbonate, dimethyl carbonate, and ethylene carbonate (1:1:1, volume percent), and the diaphragm was polypropylene film (Celgard 2320). CVs and EIS were tested on the electrochemical workstation of CHI660D. Galvanostatic charge/discharge and cycling performance were tested using an NEWARE battery measuring tester.

#### 2.3. Measurement and characterization

The morphologies and structure of the Fe-GaN nanowires were analyzed via field emission–scanning electron microscopy (SEM, Hitachi S-4800) and transmission electron microscopy (TEM, JEOL JEM-2100, 200 kV). The X-ray diffraction (XRD) patterns of the intrinsic GaN and Fe-GaN nanowires were analyzed on a Bruker diffractometer (Bruker D8). The chemical and bonding states of Fe doping were analyzed using XPS (Thermo ESCALAB 250).

#### 2.4. DFT calculation

The GaN adopted a  $3 \times 3 \times 1$  supercell, including 18 Ga atoms and 18 N atoms(Fig. 5a). One Fe atom instead of one Ga atom in the Fe-GaN. The (001) face was used in the study. A vacuum space of 15 Å was applied in the direction normal to the GaN slabs to avoid interactions between two layers. Geometrical optimization and transformation pathways were calculated on CASTEP software by using OTFG ultrasoft pseudopotentials (Delley, 1990; McNellis et al., 2009; Perdew et al., 1996). All kinds of calculations were performed via Perdew-Burke-Ernzerhof method within the generalized gradient approximation. The energy convergence standard was  $10^{-5}$  eV/atom, and the forces were 0.03 eV/Å in the structural relaxation. Moreover, the cutoff energy was set to 400 eV, and the k-point of the Brillouin zone was sampled using  $3 \times 3 \times 1$ . SCF tolerance was  $10^{-6}$  eV/atom. For the calculation of the electronic and optical properties, the cutoff energy was set to 600 eV and k-point was set to  $6 \times 6 \times 1$  to achieve high accuracy. Transformation pathways were calculated using the complete linear synchronous transit method.

#### 3. Results and discussion

Intrinsic and Fe-GaN free-standing nanowires were prepared via facile CVD. Ga<sub>2</sub>O<sub>3</sub> and NH<sub>3</sub> were the source materials, while Fe(NO<sub>3</sub>)<sub>2</sub> was the doping source. Fig. 1a clearly displays the morphology of the as-obtained Fe-GaN nanowire arrays. As shown in Fig. 1b, the single Fe-GaN nanowire had a smooth surface. The elemental disperse spectroscopy analysis (EDS) in Fig. 1c showed that Ga, Fe, C, and N coexisted in the Fe-GaN nanowires. Owing to the existence vapor of Ga and Fe at 1100 °C, Fe element can uniformly disperse in the GaN nanowires at room temperature. Therefore, as shown in Fig. 1g, elemental mapping analyses illustrated the uniform distribution of Fe, Ga, and N. The average concentration of Fe in the Fe-GaN nanowire was approximately 1.5% (atomic percent), as shown in the quantitative elemental analysis results, which were consistent with the XPS analysis results (Fig. 2b). Further information was obtained from the TEM result to analyze the crystal phase information of the Fe-GaN nanowires. Fig. 1d and e show that the diameter was 50 nm, which was well consistent with the SEM result. The high-resolution TEM image showed the well-crystallized structure of the Fe-GaN nanowire with high crystallinity, and the lattice fringe spacing was 2.76 Å, corresponding to the (100) lattice plane of the wurtzite GaN. In the inset of Fig. 1f, the SAED result unambiguously showed the [100] growth direction of Fe-GaN nanowires, indicating that the Fe dopant had a negligible effect on the Fe-GaN nanowire growth (Sun et al., 2018). Moreover, the crystallinity of electrode materials is vital to the performance LIB anodes (Ding et al., 2016).

As shown in Fig. 2a, the XRD patterns of the Fe-doped GaN could be directly assigned as wurtzite GaN (JCPDS: No. 50-0792). The diffraction peak intensity and position

almost did not change compared with those of the intrinsic GaN nanowires, indicating the limited influence of heteroatom doping. XPS measurements were conducted to analyze the valence state of Ga, Fe, and N in the intrinsic and Fe-GaN nanowires. In Fig. 2b, the Fe 2p peaks were located at 708.6 and 721.3 eV, corresponding to the  $2p_{1/2}$  and  $2p_{3/2}$  valence states of the Fe<sup>2+</sup> ions, respectively. The chemical bonding located at 710.2 and 723.8 eV was related to the  $2p_{1/2}$  and  $2p_{3/2}$  valence states of the Fe<sup>3+</sup> ions, respectively (Huang et al., 2016). No other peaks, such as Ga-Fe or Fe-Fe peaks, were observed in the Fe 2p spectrum, indicating that no other impurities were present in the Fe-GaN nanowires. Moreover, the Fe 2p spectrum revealed that  $Fe^{2+}$  and  $Fe^{3+}$  ions coexisted in the Fe-GaN nanowires. The Ga 3d high-resolution XPS spectra of the intrinsic and Fe-GaN nanowires were provided. As shown in Fig. 2c, Ga-O (17.8 eV) and Ga-N (19.5 eV) bonds were observed in the intrinsic and Fe-GaN nanowires (Khir et al., 2014). The existence of Ga-O bonds could be ascribed to the much higher thermodynamic barriers of N $\equiv$ N bonds (945 kJ mol<sup>-1</sup>) than those of O $\equiv$ O bonds (498 kJ mol<sup>-1</sup>), which lead to the inevitable oxidation during the formation of the Fe-GaN nanowires (Balogun et al., 2015). The weakened Ga-O peak in the Fe-GaN nanowires indicated the decrease in the O content in the Fe-GaN nanowires compared with that in the intrinsic GaN nanowires. Moreover, the binding energy of the Ga 3d core level in Fe-GaN was shifted to a lower energy compared with that in the intrinsic GaN. This phenomenon could be attributed to the weaker electronegativity of the Fe atom, resulting in the increase in electron density of the Fe-GaN nanowires. Fig. 2d illustrates that the N peak was located at 397.8 eV, which could be assigned to the N-Ga bond in the intrinsic GaN and Fe-GaN (Jung et al., 2019). The N-Fe peak (398 eV) could not be separated in the Fe-GaN nanowires due to the highly overlapped N-Ga and N-Fe bonds (Yu et al., 2019; Liu et al., 2019). Besides; the electrical conductivity result showed that the conductivity of Fe-GaN nanowire  $(3.5 \times 10^3 \text{ S m}^{-1})$  was much higher than that of intrinsic GaN nanowire (Sun et al., 2018). The conductivity of graphite layer was  $\sim 8.6 \times 10^4 \text{ S} \cdot \text{m}^{-1}$ . The excellent electrical conductivities of Fe-GaN and graphite substrate ensured efficient charge transfer and excellent electrochemical performance (Chan et al., 2008).

The intrinsic GaN and Fe-GaN electrodes were studied as anodes in the coin-type half cells for LIBs, and the electrochemical performances were determined. Fig. 3a shows the CV curves of the Fe-GaN electrode at  $0.1 \text{ mV s}^{-1}$ , which could obtain an unambiguous insight of the electrochemical reaction mechanism. In the first cycle process, the peak (~0.45 V) can be attributed to the formation of solid electrolyte interphase (SEI) (Lee et al., 2013). The Li<sup>+</sup> insertion peaks of Fe-GaN electrode in the CVs (Fig. 3a) remained stable except the first cycle, indicating the increased structural stability of the Fe-GaN nanowires (Wu et al., 2011). In the next cycling, the Li<sup>+</sup> insertion peaks that appeared in the first cycle disappeared, and a broad peak at ~0.9 V appeared, indicating the electrochemical reaction of Li<sup>+</sup> with the metal nitrides (Sato et al., 1994; Lee et al., 2013). In the Li<sup>+</sup> insertion and desertion processes, the peak at 0.5-1.2 V was related to the reversible Li<sup>+</sup> desertion reaction in the Fe-GaN nanowires. The peak at 0.9 V still was discernable until the 10th cycle, indicating the high structural stability of Fe-GaN nanowires in the electrochemical



**Fig. 1** Morphological characterization of Fe-GaN nanowires. (a) Low-resolution SEM. (b, c) SEM image and EDS analysis of single nanowire. (d, e) Low-resolution TEM. (f) HRTEM image of nanowire with (100) plane; the top left inset was the SAED pattern. (g) SEM image and corresponding elemental mapping analysis of nanowires.



**Fig. 2** (a) X-ray power diffraction (XRD) analysis of the intrinsic GaN and Fe-GaN. (b) Fe 2p XPS spectra and corresponding fitting results of the Fe-GaN nanowires. Comparison XPS spectra of (c) Ga 3d and (d) N 1s of the intrinsic and Fe-GaN nanowires.



**Fig. 3** (a) CV curve of Fe-GaN nanowires electrode at 0.1 mV s<sup>-1</sup> within 0.01–3 V. (b) Charge and discharge curves and (c) cycling capabilities of Fe-GaN at 0.1 A g<sup>-1</sup>. (d) Rate property of intrinsic GaN and Fe-GaN nanowires. (e) Cycling property of Fe-GaN at 5.0 A  $g^{-1}$ .

reaction. Except for the first cycle, the CVs overlapped in the second, fifth, and 10th cycles, indicating the highly reversible  $Li^+$  insertion and desertion processes in the Fe-GaN nanowire electrodes. In the next cycles,  $Li^+$  insertion and desertion peaks of the CVs became stable, indicating that the electrochemical reaction was highly reversible. Although  $Li^+$  insertion and desertion peaks slightly shifted, the shape of the CVs in the intrinsic and Fe-GaN electrodes was similar, indicating a stable  $Li^+$  storage mechanism in the Fe-GaN nanowire electrodes (Sun et al., 2018). Therefore, the CVs result reveals the reversible  $Li^+$  intercalation mechanism of Fe-GaN nanowires. The stable platform and  $Li^+$  storage performances were also studied in the galvanostatic discharge and charge curves at 0.1 A g<sup>-1</sup> (Fig. 3b). In the first cycle, the discharge and charge

capacities were 925.6 and 646.7 mAh g<sup>-1</sup>, respectively, while the Coulombic efficiency was 69.8%. For Fe-GaN nanowires electrode, Fe doping enhanced electrical conductivity and charge-transfer efficiency, the pulverization phenomenon is negligible. Therefore, the irreversible capacity loss and lower initial coulombic efficiency could be attributed to the solid electrolyte interphase (SEI) layer in the first cycle (Sun et al., 2018). From the second cycle to the 100th cycle, the charge and discharge curves almost overlapped, and the irreversible capacity loss decreased. The high Li<sup>+</sup> storage reversibility and structural stability of the Fe-GaN nanowires is consistent well with the CV results in Fig. 3a (Zhou et al., 2015).

well with the CV results in Fig. 3a (Zhou et al., 2015). After 200 cycles at 0.1 A  $g^{-1}$ , the corresponding discharge capacity was 612.3 mAh  $g^{-1}$ , and it retained approximately 100% Coulombic efficiency, as shown in Fig. 3c. However, for the intrinsic GaN electrode, the discharge capacity could be maintained at 490 mA h  $g^{-1}$  (Sun et al., 2018); which was inferior to that of the Fe-GaN electrode. Therefore, Fe doping enhanced the ionic transfer efficiency and electrical conductivity and subsequently boost the lithiation and delithiation reactions and Li<sup>+</sup> storage performance. The rate capabilities were compared because rate performance represents the advantages of Li<sup>+</sup> storage performance, as shown in Fig. 3d. As the current density increased, the Fe-GaN nanowire electrode exhibited ultra-stable and reversible rate capacities of 629.4, 542.7, 467.7, 379.6, and 325.6 mAh  $g^{-1}$  at 0.1, 0.3, 0.5, 2.0, and 5.0 A  $g^{-1}$ , respectively. For the intrinsic GaN electrode, the rate capability was much inferior, indicating seriously limited Li<sup>+</sup> diffusion in the intrinsic GaN. When the rate was returned to 0.1 A g<sup>-1</sup>, the rate capacity of the Fe-GaN nanowire electrode also returned to 603.5 mAh  $g^{-1}$ , indicating stable Li<sup>+</sup> insertion/extraction reactions, decreased pulverization phenomenon, and the structure stability of the Fe-GaN nanowires. Therefore, Fe doping could improve electrical conductivity and boost Li<sup>+</sup> storage performance (Li et al., 2019). For an enhanced understanding of the favorable electrochemical performance, the long-term cycling property was measured at 5.0 A  $g^{-1}$  (Fig. 3e). In the initial 10 cycles, the discharge capacity showed a gradual decrease from 874.2 mAh  $g^{-1}$  to 358.7 mAh  $g^{-1}$ . Then, it became stable from the 11th cycle, and the Fe-GaN nanowire electrode showed outstanding electrochemical stability under a large current density. After

500 cycles, the reversible discharge capacity could still be maintained at 338.2 mAh g<sup>-1</sup> with approximately 100% Coulombic efficiency. The discharge capacity retention was approximately 82.4% (relative to the second discharge capacity). The long cycling property of intrinsic GaN nanowires was also tested at 5.0 A  $g^{-1}$  (Fig. S1). After 500 cycles, this hybrid electrode still maintained reversible discharge capacity of 153.2 mAh  $g^{-1}$ . These excellent capacity retention and structural stability showed highly reversible Li<sup>+</sup> insertion and extraction reaction kinetics (Ding et al., 2016). Moreover, the average capacity fading in the Fe-GaN electrode was approximately 0.035% per cycle. Thus, Fe-GaN obviously showed higher cycling stability than intrinsic GaN. This finding could be attributed to the well electrical conductivity, charge-transfer efficiency, and structural stability. To more clearly illustrate electrochemical performances of Fe-GaN nanowires electrode, Table S1 list the compared morphologies, cycle numbers, current densities, and capacities with those of other previously reported semiconductor-based anodes. It can be found that the Fe-GaN nanowires electrode has a superior structural tolerance during the Li<sup>+</sup> insertion and extraction processes.

To probe the effects of Fe doping, electrochemical impedance spectroscopy (EIS) measurements are performed from 100 kHz to 0.01 Hz. In Fig. S2, the EIS plots of the intrinsic GaN and Fe-GaN electrodes contain the semicircles in the range of high-to-medium frequencies and the inclined line at low frequencies, which can be ascribed to the charge-transfer



**Fig. 4** Kinetic analysis of the electrochemical behavior of Fe-GaN nanowire electrode. (a) CVs from 0.1 mV s<sup>-1</sup> to 1.0 mV s<sup>-1</sup>. (b) *b* value determined via Log i versus Log v plots. (c) Normalized radios of diffusion capacities from 0.1 mV s<sup>-1</sup> to 1.0 mV s<sup>-1</sup>. (d) Determined capacitive and diffusion contributions of Fe-GaN electrode at 1.0 mV s<sup>-1</sup>.

resistances (R<sub>ct</sub>) at the interfaces and in a mass-transfer process, respectively. By comparison, the R<sub>ct</sub> of the Fe-GaN electrode (146.8  $\Omega$ ) is significantly less than that of intrinsic GaN electrode (183.7  $\Omega$ ), suggesting the higher charge-transfer rate and superior electrochemical performance of the Fe-GaN electrode. Furthermore, the slope of Fe-GaN electrode in the lowfrequency region is much higher than intrinsic GaN, confirming the better mobility of Li<sup>+</sup> and pore structure/path in the Fe-GaN electrode. A detailed kinetic study of the Fe-GaN nanowire electrode was performed to further explore the reason for the excellent rate capability. In Fig. 4a, the CVs showed similar shapes with the broaden lithiation and delithiation peaks. The negligible peak change indicated the well reversibility, fast charge transfer, and low polarization processes in the doped GaN nanowire electrode (Xia et al., 2016). In accordance with  $i = av^b$ ; where a and b are constants, and i and v are the measured current and scan rate, respectively, the capacitive and diffusion contributions were quantitatively analyzed. The b values for the diffusion and capacitance processes were 0.5 and 1.0, respectively (Wang et al., 2017). As shown in Fig. 4b; the b values of the O1, O2, and R peaks were 0.93, 087, and 0.82, respectively, indicating that capacitive and diffusion contributions coexisted in the Fe-GaN nanowire electrode (Chao et al., 2016). Capacitive  $(k_1v)$  and diffusion  $(k_2v^{1/2})$  contributions could be quantitatively separated according to Dunn's work (Brezesinski et al., 2010). As shown in Fig. 4c, the pseudocapacitive behavior increased as the scan rates increased, whereas the diffusion controlled process declined. Fig. 4d demonstrates that the separated capacitive contribution was 82.4% of the total capacity at 1.0 mV s<sup>-1</sup>. For intrinsic GaN nanowire electrode, the separated capacitive contribution was 78.6% at 1.0 mV s<sup>-1</sup> (Sun et al., 2018). The difference of the pseudocapacitance between GaN and Fe-GaN nanowires can be attributed to the microstructure change of the Fe-GaN nanowires after Fe doping. Moreover, the diffusion process occurred at the peak region, indicating that this process is feasible at the peak region (Chen et al., 2015).

DFT calculations were further conducted to analyze the electrical conductivity and Li<sup>+</sup> storage kinetics enhanced after



**Fig. 5** (a) Optimized structure model of intrinsic GaN and Fe-GaN. (b, c) Electron density differences of pristine GaN and Fe-GaN. Calculated band structure of (d) pristine GaN and (e) Fe-GaN. (f) Partial density of the states of pristine GaN and Fe-GaN. The Fermi level is defined as zero. (g, h) Schematic and energy profiles of the Li migration pathway in GaN and Fe-GaN.

Fe doping in the Fe-GaN nanowires. Fig. 5a shows the structure of the intrinsic and Fe-GaN with the bond length. Overall, the bond length of Fe-GaN was smaller and the bond angle was larger than those of the intrinsic GaN. These results indicated that Fe doping could regulate the Fe-GaN crystal structure, which determines electrical conductivity and Li<sup>+</sup> absorption and desorption (Wu et al., 2018). The charge density differences of the intrinsic GaN and Fe-GaN (Fig. 5b and c) were determined to explore the effects of Fe dopants in the nearby atoms. The charge recombination made the changes in local charge distribution possible, thereby leading to accelerated charge carriers in Fe-GaN. Moreover, the doped Fe atoms demonstrated an decrease in negative charge with the decrease in charge density, whereas the charge density of the nearby atoms increased. Fig. S3 showed the calculated 3D charge density difference. The yellow regions were the enriched charge, and they were mainly distributed on N atom, the blue regions indicated charge depletion located at Fe atom. The calculated density of states (DOS) of the pristine GaN and Fe-GaN (Fig. 5f) showed that Fe-GaN had higher DOS at the Fermi level than the pristine GaN, indicating that Fe doping could improve electrical conductivity, and the doped Fe atoms, as active sites, improved the performance of GaN. The band structures (Fig. 5d and e) also indicated that Fe remarkably improved the electrical conductivity of GaN by decreasing its band gap because of the contributions of 3d orbitals in the Fe atom. A schematic of the Li<sup>+</sup> migration pathway is illustrated in Fig. 5g to clarify the effects of the Fe atom in Li<sup>+</sup> migration. The energy profiles of this pathway are shown in Fig. 5h, and the energy barrier in the pristine GaN was 1.4 eV. However, when the Fe atoms were introduced, the energy barrier was as small as 0.43 eV, indicating that the migration energy barrier of Li<sup>+</sup> was much lower in the Fe-GaN system. These theoretical results suggested that foreign doping played a key role in tuning the electronic structure and improving the Li<sup>+</sup> storage performance of LIB anodes.

#### 4. Conclusion

In summary, Fe-GaN nanowires were prepared and studied as electrodes of LIBs. Benefiting from the sufficient electronic structure engineering and improved electrical conductivity, the optimized Fe-GaN nanowire electrode showed observably enhanced Li<sup>+</sup> storage performance (612.3 mAh g<sup>-1</sup> at 0.1 A g<sup>-1</sup> after 200 cycles and 338.2 mAh g<sup>-1</sup> at 5.0 A g<sup>-1</sup> after 500 cycles). DFT results showed that Fe doping could significantly enhance the electrical conductivity and Li<sup>+</sup> activity via electrical conductivity and desorption analysis showed that Fe doping accelerated the Li<sup>+</sup> insertion and desertion processes, with decreased diffusion barrier. This electron density strategy of foreign atom doping could provide available references for the improvement of the electrochemical properties of LIBs.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgements

The work reported here was supported by the National Natural Science Foundation of China under Grant No. 51602168, the Tianyou Youth Talent Lift Program of Lanzhou Jiaotong University, the Joint Innovation Fund Program of Lanzhou Jiaotong University-Tianjin University under Grant No. 2019055, the Guangdong Basic and Applied Basic Research Foundation (2019A1515110933), China Postdoctoral Science Foundation (Grant No. 2020M683450) and Shandong Provincial Universities Young Innovative Talent Incubation Program-Inorganic Non-metallic Materials Research and Innovation Team. Computations were done using National Supercomputing Center in Shenzhen, P. R. China.

#### Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.arabjc.2021.103161.

#### References

- Ali, G., Lee, J.-H., Oh, S.H., Jung, H.-G., Chung, K.Y., 2017. Nano Energy 42, 106–114.
- Baggetto, L., Verhaegh, N.A.M., Niessen, R.A.H., Roozeboom, F., Jumas, J.-C., Notten, P.H.L., 2010. J. Electrochem. Soc. 157, A340–A347.
- Balogun, M.-S., Yu, M., Huang, Y., Li, C., Fang, P., Liu, Y., Lu, X., Tong, Y., 2015. Nano Energy 11, 348–355.
- Balogun, M.-S., Qiu, W., Wang, W., Fang, P., Lu, X., Tong, Y., 2015. J. Mater. Chem. A 3, 1364–1387.
- Brezesinski, T., Wang, J., Tolbert, S.H., Dunn, B., 2010. Nat. Mater. 9, 146.
- Chan, C.K., Peng, H., Liu, G., McIlwrath, K., Zhang, X.F., Huggins, R.A., Cui, Y., 2008. Nat. Nanotechnol. 3, 31–35.
- Chao, D., Liang, P., Chen, Z., Bai, L., Shen, H., Liu, X., Xia, X., Zhao, Y., Savilov, S.V., Lin, J., Shen, Z.X., 2016. ACS Nano 10, 10211–10219.
- Chen, C., Wen, Y., Hu, X., Ji, X., Yan, M., Mai, L., Hu, P., Shan, B., Huang, Y., 2015. Nat. Commun. 6, 6929.
- Delley, B., 1990. J. Chem. Phys. 92, 508-517.
- Ding, Y., Cano, Z.P., Yu, A., Lu, J., Chen, Z., 2019. Electrochem. Energy Rev. 2, 1–28.
- Ding, Y.L., Kopold, P., Hahn, K., van Aken, P.A., Maier, J., Yu, Y., 2016. Adv. Mater. 28, 7774–7782.
- Dou, F., Shi, L., Chen, G., Zhang, D., 2019. Electrochem. Energy Rev. 2, 149–198.
- Fu, Z.-W., Wang, Y., Yue, X.-L., Zhao, S.-L., Qin, Q.-Z., 2004. J. Phys. Chem. B 108, 2236–2244.
- González-Macías, A., Salazar, F., Miranda, A., Trejo-Baños, A., Pérez, L.A., Carvajal, E., Cruz-Irisson, M., 2018. Nanotechnology 29, 154004.
- Han, J., Wei, W., Zhang, C., Tao, Y., Lv, W., Ling, G., Kang, F., Yang, Q.-H., 2018. Electrochem. Energy Rev. 1, 139–168.
- He, H., Huang, D., Tang, Y., Wang, Q., Ji, X., Wang, H., Guo, Z., 2019. Nano Energy 57, 728–736.
- Huang, Y., Lin, Z., Zheng, M., Wang, T., Yang, J., Yuan, F., Lu, X., Liu, L., Sun, D., 2016. J. Power Sources 307, 649–656.
- Huang, L., Waller, G.H., Ding, Y., Chen, D., Ding, D., Xi, P., Wang, Z.L., Liu, M., 2015. Nano Energy 11, 64–70.
- Huang, L., Lin, S., Xu, Z., Zhou, H., Duan, J., Hu, B., Zhou, J., 2020. Adv. Mater. 32, 1902034.
- Jung, J.-W., Kim, C., Cheong, J.Y., Kim, I.-D., 2019. ACS Appl. Mater. Interfaces 11, 44263–44269.

- Khir, F.L.M., Myers, M., Podolska, A., Sanders, T.M., Baker, M.V., Nener, B.D., Parish, G., 2014. Appl. Surf. Sci. 314, 850–857.
- Lai, L., Zhu, J., Li, B., Zhen, Y., Shen, Z., Yan, Q., Lin, J., 2014. Electrochim. Acta 134, 28–34.
- Lee, S., Sridhar, V., Jung, J., Karthikeyan, K., Lee, Y., Mukherjee, R., Koratkar, N., Oh, I., 2013. ACS Nano 7, 4242–4251.
- Li, Y., Cao, C., Chen, Z., 2010. J. Phys. Chem. C. 114, 21029-21034.
- Li, Z., Ding, S., Yin, J., Zhang, M., Sun, C., Meng, A., 2020. J. Power Sources 451, 227815.
- Li, Y., Guo, S., Jin, T., Wang, Y., Cheng, F., Jiao, L., 2019. Nano Energy 63, 103821.
- Li, W., Li, X., Yu, J., Liao, J., Zhao, B., Huang, L., Ali, A., Zhang, H., Wang, J.H., Guo, Z., Liu, M., 2019. Nano Energy 61, 594–603.
- Li, L., Zhang, X., Li, M., Chen, R., Wu, F., Amine, K., Lu, J., 2018. Electrochem. Energy Rev. 1, 461–482.
- Li, Y., Zhang, R., Zhou, W., Wu, X., Zhang, H., Zhang, J., 2019. ACS Nano 13, 5533–5540.
- Liu, Y., Chen, Z., Jia, H., Xu, H., Liu, M., Wu, R., 2019. ACS Nano 13, 6113–6124.
- Liu, C., Li, F., Ma, L.P., Cheng, H.M., 2010. Adv. Mater. 22, E28– E62.
- Liu, D., Xu, X., Tan, J., Zhu, J., Li, Q., Luo, Y., Wu, P., Zhang, X., Han, C., Mai, L., 2019. Small 15, 1803572.
- Liu, B., Zhang, J., Wang, X., Chen, G., Chen, D., Zhou, C., Shen, G., 2012. Nano Lett. 12, 3005–3011.
- Lu, J., Chen, Z., Pan, F., Cui, Y., Amine, K., 2018. Electrochem. Energ. Rev. 1, 35–53.
- Ma, Y., Ma, Y., Giuli, G., Euchner, H., Groß, A., Lepore, G.O., d'Acapito, F., Geiger, D., Biskupek, J., Kaiser, U., Schütz, H.M., Carlsson, A., Diemant, T., Behm, R.J., Kuenzel, M., Passerini, S., Bresser, D., 2020. Adv. Energy Mater. 10, 2000783.
- McNellis, E.R., Meyer, J., Reuter, K., 2009. Phys. Rev. B 80, 205414.
- McNulty, D., Biswas, S., Garvey, S., O'Dwyer, C., Holmes, J.D., 1819. ACS Appl. Energy Mater. 3 (2020), 11811–11821.
- Mueller, F., Bresser, D., Chakravadhanula, V.S.K., Passerini, S., 2015. J. Power Sources 299, 398–402.
- Ni, S., Huang, P., Chao, D., Yuan, G., Zhang, L., Zhao, F., Li, J., 2017. Adv. Funct. Mater. 27, 1701808.
- Peng, Q., Lie, Y., Tang, Z., Sun, C., Li, J., Wu, G., Wang, T., Yin, Z., Liu, H., 2020. Electrochim. Acta 350, 136380.
- Perdew, J.P., Burke, K., Ernzerhof, M., 1996. Phys. Rev. Lett. 77, 3865–3868.
- Pereira, N., Klein, L.C., Amatucci, G.G., 2002. J. Electrochem. Soc. 149, A262–A271.
- Raman, K.H.T., Penki, T.R., Munichandraiah, N., Rao, G.M., 2014. Electrochim. Acta 125, 282–287.
- Rodriguez, J.R., Qi, Z., Wang, H., Shalaginov, M.Y., Goncalves, C., Kang, M., Richardson, K.A., Guerrero-Sanchez, J., Moreno-Armenta, M.G., Pol, V.G., 2020. Nano Energy 68, 104326.
- Santiago, F.D., González, J.E., Miranda, A., Trejoa, A., Salazar, F., Pérez, L.A., Cruz-Irisson, M., 2019. Energy Storage Mater. 20, 438–445.
- Sato, K., Noguchi, M., Demachi, A., Oki, N., Endo, M., 1994. Science 264, 556–558.

- Seong, H.K., Kim, J.Y., Kim, J.J., Lee, S.C., Kim, S.R., Kim, U., Park, T.E., Choi, H.J., 2007. Nano Lett. 7, 3366–3371.
- Snyder, M.Q., Trebukhova, S.A., Ravdel, B., Wheeler, M.C., DiCarlo, J., Tripp, C.P., DeSisto, W.J., 2007. J. Power Sources 165, 379–385.
- Sun, Q., Fu, Z.-W., 2012. Appl. Surf. Sci. 258, 3197–3201.
- Sun, C., Yang, M., Wang, T., Shao, Y., Wu, Y., Hao, X., 2017. ACS Appl. Mater. Interfaces 9, 26631–26636.
- Sun, C., Yang, M., Wang, T., Shao, Y., Wu, Y., Hao, X., 2018. ACS Appl. Mater. Interfaces 10, 2574–2580.
- Sun, C., Tang, X., Yin, Z., Liu, D., Wang, Y.-J., Yang, G., Ignaszak, A., Zhang, J., 2020. Nano Energy 68, 104376.
- Tan, S.-J., Zeng, X.-X., Ma, Q., Wu, X.-W., Guo, Y.-G., 2018. Electrochem. Energy Rev. 1, 113–138.
- Tang, C., Wang, H.-F., Huang, J.-Q., Qian, W., Wei, F., Qiao, S.-Z., Zhang, Q., 2019. Electrochem. Energy Rev. 2, 332–371.
- Vishnu, D.S.M., Sure, J., Kim, H., Kumar, R.V., Schwandt, C., 2020. Energy Storage Mater. 26, 234–241.
- Wang, T., Zhao, G., Sun, C., Zhang, L., Wu, Y., Hao, X., Shao, Y., 2017. Adv. Mater. Interfaces 4, 1601187.
- Wang, T., Sun, C., Yang, M., Zhao, G., Wang, S., Ma, F., Zhang, L., Shao, Y., Wu, Y., Huang, B., Hao, X., 2017. J. Alloys Compd. 716, 112–118.
- Wang, T., Sun, C., Yang, M., Zhang, L., Shao, Y., Wu, Y., Hao, X., 2018. Electrochim. Acta 259, 1–8.
- Wu, Y., Liu, X., Han, D., Song, X., Shi, L., Song, Y., Niu, S., Xie, Y., Cai, J., Wu, S., Kang, J., Zhou, J., Chen, Z., Zheng, X., Xiao, X., Wang, G., 2018. Nat. Commun. 9, 1425.
- Wu, J., Luo, N., Huang, S., Yang, W., Wei, M., 2019. J. Mater. Chem. A 7, 4574–4580.
- Wu, F., Tan, G., Chen, R., Li, L., Xiang, J., Zheng, Y., 2011. Adv. Mater. 23, 5081–5085.
- Xia, X., Chao, D., Zhang, Y., Zhan, J., Zhong, Y., Wang, X., Wang, Y., Shen, Z.X., Tu, J., Fan, H.J., 2016. Small 12, 3048–3058.
- Xiang, H.J., Wei, S.-H., 2008. Nano Lett. 8, 1825–1829.
- Xu, G., Zhang, L., Guo, C., Gu, L., Wang, X., Han, P., Zhang, K., Zhang, C., Cui, G., 2012. Electrochim. Acta 85, 345–351.
- Yang, M., Sun, C., Wang, T., Chen, F., Sun, M., Zhang, L., Shao, Y., Wu, Y., Hao, X., 2018. ACS Appl. Energy Mater. 1, 4708–4715.
- Yang, Y., Yuan, W., Kang, W., Ye, Y., Pan, Q., Zhang, X., Ke, Y., Wang, C., Qiu, Z., Tang, Y., 2020. Sustain. Energy Fuels 4, 1577– 1594.
- Yu, L., Song, S., McElhenny, B., Ding, F., Luo, D., Yu, Y., Chen, S., Ren, Z., 2019. J. Mater. Chem. A 7, 19728–19732.
- Zhang, X., Jin, L., Dai, X., Chen, G., Liu, G., 2018. ACS Appl. Mater. Interfaces 10, 38978–38984.
- Zhang, X., Chen, A., Zhong, M., Zhang, Z., Zhang, X., Zhou, Z., Bu, X.-H., 2019. Electrochem. Energy Rev. 2, 29–104.
- Zhou, J., Qin, J., Zhang, X., Shi, C., Liu, E., Li, J., Zhao, N., He, C., 2015. ACS Nano 9, 3837–3848.
- Zhou, J., Jiang, F., Li, S., Zhao, W., Sun, W., Ji, X., Yang, Y., 2019. Electrochim. Acta 321, 134676.
- Zhou, K., Zhou, W., Liu, X., Sang, Y., Ji, S., Li, W., Lu, J., Li, L., Niu, W., Liu, H., Chen, S., 2015. Nano Energy 12, 510–520.