Surface thermodynamic stability of Li-rich Li$_2$MnO$_3$: Effect of defective graphene

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**Abstract**

Li-rich Mn-based cathode materials used in Li-ion batteries show ultra-high capacity due to the favorable oxygen redox behavior induced by activation of Li$_3$MnO$_2$. However, structural degradation associated with oxygen loss and transition metal migration occurs due to excessive oxygen redox on the surface, which is the main origin of the low coulombic efficiency, capacity fade, and voltage decay, which limit the widespread application of this high-capacity material. In this study, the underlying mechanism of tuning the surface thermodynamic stability of the Li$_2$MnO$_3$ model material was systematically investigated. The results showed that a defective graphene coating can effectively stabilize surface oxygen by modification of the potential energy surface, while reducing Mn migration and increasing the diffusivity of Li ions. Theoretical calculations predicted an improvement in the electrochemical performance, which was confirmed by experimental results. These findings may provide a novel strategy for increasing the surface thermodynamic stability of electrode materials.

1. Introduction

Li-rich cathode materials can deliver extremely high capacity for lithium-ion battery applications, which results from the oxygen redox reaction induced by the activation of the Li$_2$MnO$_3$ component [1–4]. As energy storage is considered to be one of the main challenges in the widespread uptake of renewable energy, such materials are expected to greatly promote the development of electric vehicles and new grid systems; hence, they have attracted considerable attention globally. However, the structural stability of these cathode materials depends on the degree of the oxygen redox. An excessive degree of oxygen redox promotes structural degradation in terms of oxygen loss and migration of transition metal ions [5]. This results in an irreversible redox reaction [6], which is reflected in the battery performance by a low initial coulombic efficiency [7], capacity fade [8], voltage decay [8,9], and poor rate capability [10]. These factors are major obstacles preventing industrial application of Li-rich Mn-based oxide in Li-ion batteries.

Previous studies demonstrated that the oxygen loss and transition metal migration always start at the surface [11–14], suggesting that structural degradation mainly results from the thermodynamic instability of the surface of the Li-rich materials, especially the Li$_2$MnO$_3$ surface [13,15,16]. Hence, extensive efforts have been made to suppress irreversible oxygen redox using methods such as doping [9,17], surface coating [13,18–21], tailoring the morphology to expose favorable dominant surface crystal facets [22,23], and fabricating nanometer-sized materials [24–27]. These strategies can modify the cycling stability of Li-rich Mn-based cathode materials to some extent, but usually reduced the capacity contributed by the oxygen redox reaction. Hence, further research is required before practical application of this material is viable.

A detailed understanding of the underlying mechanism of the reversibility of oxygen redox is important for determining appropriate methods for enhancing the electrochemical performance of Li-rich Mn-based cathode materials. Here, we have analyzed the factors affecting the thermodynamic stability of oxygen on the surface of Li-rich materials during delithiation based on first-principles calculations using the Li$_2$MnO$_3$ model structure. We found that defective graphene could effectively modify the potential energy surface of Li$_2$MnO$_3$ and thus enhance the surface stability by suppressing oxygen loss and limiting Mn migration, while having little effect on the capacity provided by surface oxygen redox. To the best of our knowledge, this is the first time to propose the critical role of potential energy surface in suppressing oxygen loss in Li-rich materials. In addition, defective graphene can improve the rate performance. Finally, experimental results confirmed that the electrochemical performance was greatly improved by the defective graphene coating.
2. Results and discussion

2.1. Oxygen thermodynamic stability of Li₂MnO₃

The low coulombic efficiency and poor capacity retention of Li-rich cathode materials during cycling were found to be associated with O₂ release due to excessive oxidation of oxygen ions upon delithiation which initially occurred at the surface [11,15,16]. However, previous work showed that the oxygen in the Li₂MnO₃ bulk can undergo reversible redox and deliver reversible capacity without oxygen loss [11,12]. This suggests that the thermodynamic stability of surface oxygen upon delithiation is a key aspect of the electrochemical performance of Li-rich cathode materials. Hence, we modeled the Li₂MnO₃ surface to study its oxygen thermodynamic stability. It has been reported that the (010) surface is one of the most prevalent facets of Li₂MnO₃ particles [15,28], while also being the active plane for Li⁺ ion diffusion [22,29]. Previous calculations of the oxygen release energy demonstrated that the (010) facet was the most unstable facet and most prone to oxygen loss among all low Miller index surfaces of Li₂MnO₃ [15]. Therefore, the (010) surface was used here to investigate the surface oxygen thermodynamic stability of Li₂MnO₃.

Fig. S1 shows the surface energy of different terminations and surface rearrangements of the (010) slab within a 1 × 1 cell. The surface energy of the Li/O-terminated surface was lower than that of the Li/Mn/O-terminated one. However, the rearrangement can reduce the surface energy when surface Mn ions exist with a less than six-fold coordination. After the exchange between the under-coordinated surface Mn and subsurface 2b site or 2c site Li, the surface energy decreased from 2.559 to 1.422 J/m² and 1.315 J/m², respectively, consistent with the reconstruction scheme within Li₂MnO₃ proposed previously [15]. Hence, the slab with Mn-Li(2b) exchange is the most stable. Thus, all calculations discussed here are based on the Mn-Li(2b) exchange system with a 2 × 2 supercell, as shown in Fig. 1(a, b).

The fully delithiated (010)-slab of Li₂MnO₃ (i.e., MnO₃) is shown in Fig. 1(c, d). It can be clearly seen that the oxygen ions on the surface approach each other after delithiation, and form O–O dimers with an O–O distance of 1.312 Å, which is close to that of 1.235 Å in the O2 molecule. The O–O dimer formation during the charging and discharging progresses agrees well with previous studies [30,31]. Fig. 1(e) shows the charge compensation from the surface to the bulk when all lithium ions are extracted from Li₃MnO₅ (evaluated using Bader charge analysis). The charge compensation can also be reflected by the band-decomposed charge density near the Fermi level of Li₃MnO₅ based on the rigid-band model, as shown in Fig. 1(f). It can be seen from the band-decomposed charge density that the charge compensation of Mn ions was negligible, while the oxygen charge compensation was extremely inhomogeneous in the (010) slab, which could be related to the different electronic structures of oxygen atoms in the bulk and surface. The Bader charge differences of oxygen ions upon delithiation were about 0.55 e/atom and up to 0.97 e/atom in the bulk and on the surface, respectively. The redox reaction in the bulk occurred to a smaller extent compared to the surface, while the surface oxygen suffers the most severely from oxidation upon delithiation; hence, surface oxygen redox is more irreversible, thus surface oxygen is much less stable than bulk oxygen.

The surface oxygen release energies (defined in the Supporting information), ΔG(ΔO release) in (010) slabs of MnO₃ and Li₂MnO₃ were −1.710 eV and 4.033 eV, respectively. The ΔG(ΔO release) value for MnO₃ was negative, while it was positive for Li₂MnO₃, suggesting that oxygen release in MnO₃ can easily occur because surface oxygen was oxidized to a large extent. Furthermore, the activation barrier for oxygen release from the MnO₃ (010) surface was only 0.13 eV, as is shown in Fig. S2; hence, surface oxygen release from this surface can easily occur from both thermodynamic and dynamic points of view. Since the internal oxygen is more stable than the surface oxygen due to differences in the electronic structure, we hypothesized that the surface oxygen could be modified to behave like the bulk oxygen, i.e., achieving reversible surface oxygen redox by tuning the surface thermodynamic stability.

2.2. Tuning of surface thermodynamic stability by defective graphene

Controlling the surface structure at the atomic scale is an important strategy for tuning the surface thermodynamic stability of Li-rich cathode materials with high capacity for Li-ion batteries. Graphene, due to its very high electronic conductivity, excellent structural stability, uniform thickness on the atomic scale, and high mechanical flexibility [32–35], is expected to have promising applications in Li-ion batteries. There exist previous reports of the application of graphene in
Li-rich cathodes [13,21,36–39], where the aim of these studies was primarily to improve the rate performance of the electrode.

Here, we explored the use of defective graphene coatings to modulate the surface stability of the material by tailoring the defect size, as shown in Fig. S3. The pores of defective graphene are terminated with V6-type defects as the size is close to the upper limit to allow ethylene carbonate molecules, the smallest molecule among common organic electrolytes, to penetrate the structure, as shown in Fig. S4. The formation energy, $\Delta E_F$, of the defective graphene coating is defined as Eq. (1) (S indicates the coated surface area). The $\Delta E_F$ values are shown in Fig. 2(a).

$$\Delta E_F = (E_{(coated Li_2MnO_3)} - E_{(Li_2MnO_3)} - E_{(Defective graphene)})^{S}$$  

The corresponding atomic structures are shown in Fig. S5 and Fig. 2(b–e). The $\Delta E_F$ values were negative for both the coated Li$_2$MnO$_3$ and coated MnO$_3$ systems; thus, energetically available defective graphene coatings were achieved on both Li$_2$MnO$_3$ and MnO$_3$. In particular, when the defective graphene was V6 type, $\Delta E_F$ was $-0.30 \text{ J/m}^2$ for MnO$_3$, which was the same as the interaction energy between the graphene layers in graphite, and close to the $\Delta E_F$ value of $-0.32 \text{ J/m}^2$ (0.02 eV/Å$^2$) for LiFePO$_4$ coated with graphene reported previously [40], indicating a stronger interaction and more stable binding for the V6-type defective graphene coating compared to pristine graphene and other defective graphene coatings. It is reasonable since the V6-type defective graphene remains two-fold-coordinated unsaturated carbon atoms. Furthermore, the $\Delta E_F$ values for the
MnO₃ cases were more negative than those for the Li₂MnO₃ ones, indicating that the coating became more stable after delithiation. The curved graphene structure shown in Fig. S5 was due to lattice mismatches between the coating layer and the Li₂MnO₃ slab. The charge redistributions after applying defective graphene coatings to Li₂MnO₃ and MnO₃ are also shown schematically in Fig. S5 and Fig. 2(b–e). Generally, the amount of charge transfer is small and interactions between the coating layer and the host material are considered to be van der Waals type. However, the V₆-type defective-graphene-coated samples showed a higher degree of charge redistribution (hence, stronger interactions) than the other cases, consistent with the formation energy results. This confirms the role of the defects in determining the coating stability when two-fold-coordinated unsaturated carbon atoms are present, as in the V₆-type defective graphene.

The ΔG(ΔO)Release values of the uncoated and coated systems are shown in Fig. 3(a). The ΔG(ΔO)Release value for the uncoated MnO₃ surface was negative, while positive values were observed after coating with both pristine and defective graphene, indicating that the coating can effectively stabilize surface oxygen. In order to understand how the defective graphene coating can prevent oxygen release on the surface, the charge compensation upon delithiation and the local atomic structure around the surface oxygen were further analyzed. The charge compensation values of the surface oxygen in the uncoated- and coated-Li₂MnO₃ systems are plotted together in Fig. 3(b) for comparison; a slight reduction in charge compensation attributed to surface oxygen redox was observed after coating. The local atomic structures of surface oxygen in corresponding delithiated states are also shown in Fig. 3(b), where the average O–O bond length at the coated surface (the specific bonds are shown in Fig. S6) increased slightly after coating. However, it should be noted that the increase in the oxygen stability evidenced by the charge compensation and local O–O bond length was weak. However, the oxygen release energy suggested that the coating had a remarkable effect on preventing surface oxygen loss; i.e., the degree of surface oxygen redox upon delithiation remained similar after coating, whereas oxygen loss was suppressed. Thus, we propose that other factors in addition to the degree of oxygen redox must exist to determine whether O₂ can be released from the surface.

In order to identify the critical factors affecting oxygen loss, we further modeled the O₂-released state by simultaneously placing the surface O–O dimer at a distance of 1 Å from the surface and shrinking the O–O bond length of an O₂ molecule in vacuum; then, the system was optimized. During the optimization, the oxygen ions tended to return to their original site and bond with Mn ions in the case of coated MnO₃ rather than trapped by pristine/defective graphene. However, the O₂ molecule tended to remain separated from the uncoated MnO₃ surface with an O–O bond length close to that of a free O₂ molecule, as shown in Fig. 3(c, d) and the videos provided in the Supporting Information. Hence, the O₂ molecule-released state in the coated system was neither stable nor metastable, and therefore could not exist. This confirms the remarkable effect of defective graphene coating on preventing surface oxygen loss. In fact, the defective graphene coating layer on the surface can change the nearby potential energy surface as the surface environment is changed by graphene coating layer. Schematic diagrams of the potential energy profile as a function of (O₂)Release position approaching the surfaces are shown in Fig. 3(c–e), while the quantitative potential energy variations are shown in Fig. S7. In the case of the uncoated MnO₃, the O₂ was released with a distance of 0.97 Å above the MnO₃ surface. The potential energy profile associated with the (O₂)Release position (blue line in Fig. 3(d)) indicated that the O₂ release state was energetically more favorable than that of surface O–O dimers bonded with Mn ions, which is consistent with the oxygen release energy results. In order to understand the potential energy surface of (O₂)Release on the pure defective graphene, the behavior of an O₂ molecule on a separate graphene layer was considered, where the O₂ molecule was adsorbed on the surface with a vertical distance of 2.93 Å; the potential energy is shown in the blue line of Fig. 3(e). In the case of the coated systems, with a distance between the MnO₃ surface and defective graphene ranging from 3.0 to 3.4 Å, the potential energy curve as a function of (O₂)Release position (blue line in Fig. 3(c)) showed that the potential energy for (O₂)Release increased over the area between the MnO₃ surface and the coating layer. This was qualitatively equivalent to the combination of the potential energy variation of the uncoated MnO₃ and the separate defective graphene layer as a function of the (O₂)Release position. Hence, from an energetic

![Fig. 4. DOS curves with the Fermi level set to 0 eV for the (a) uncoated Li₂MnO₃, (b) pristine graphene-coated, and (c) DV-type defective-, (d) V₄-type defective-, (e) V₆-type defective-graphene-coated Li₂MnO₃. Energy profiles for Li ion diffusion through the coating layer in the (f) pristine-graphene-coated, and (g) DV-type defective-, (h) V₄-type defective-, and (i) V₆-type defective-graphene-coated systems.](image-url)
point of view, we concluded that O$_2$ release could be effectively suppressed by the defective graphene coating. This clarifies the mechanism for the prevention of surface oxygen loss by the defective graphene coating via modification of the potential energy surface; simultaneously, the degree of oxygen redox remained. We predict that the cycling stability should increase after coating with the defective graphene.

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2.3. Mn ion migration

The transformation from a layered to spinel-like phase due to Mn ion migration to the Li layer after delithiation is the main cause of voltage decay in Li-rich cathode materials [14,41]. As the phase transition associated with Mn migration starts from the surface regions [11–14], it is important to understand the surface Mn ion migration in Li$_2$MnO$_3$. The Mn ion migration within the surface region was studied using NEB methods. The activation barrier for Mn migration in the uncoated MnO$_2$ was 0.36 eV, as shown in Fig. 3(a), indicating that Mn ions can easily migrate. The energy profiles for Mn migration and the corresponding migration path are shown in Fig. S8(a) and (b). In contrast, the activation barriers of $\sim$2 eV were quite high for the defective-graphene-coated systems, as shown in Fig. 3(a) and Fig. S8(c–f), indicating that Mn migration was suppressed by the coating, especially the defective graphene coating. Therefore, the voltage decay of Li-rich cathode materials is expected to be substantially suppressed by defective graphene coatings.

During migration of surface Mn ions, the O–O dimer originally bonded with the migrating Mn eventually formed an O$_2$ molecule. Thus, Mn ion migration is coupled with O$_2$ release, as is proposed in previous works that Mn ion migration is induced by oxygen release [14,42,43]. The high activation barrier for Mn migration in the defective-graphene-coated system can therefore be attributed to stabilization of the surface oxygen due to the presence of defective graphene.

2.4. Electronic and ionic conductivity in defective-graphene-coated Li$_2$MnO$_3$

Both the electronic and ionic conductivity play important roles in the performance of electrode materials. Considering the excellent electronic conductivity of graphene, the overall electronic conductivity is expected to increase after coating the Li$_2$MnO$_3$ with defective graphene. The calculated DOS of uncoated Li$_2$MnO$_3$ and MnO$_2$ shown in Fig. S9 indicate the rigid-hand behavior as the DOS of MnO$_2$ can be referred from that of Li$_2$MnO$_3$. Fig. S9 also showed that the electronic structure of MnO$_2$ was metallic, indicating that the electronic conductivity of Li$_2$MnO$_3$ increased after delithiation, which was confirmed by a previous study [29]. Therefore, the poor electronic conductivity was mainly related to the lithiated state, especially for stoichiometric Li$_2$MnO$_3$. Thus, the DOS of the uncoated Li$_2$MnO$_3$ and defective-graphene-coated system were studied, as shown in Fig. 4(a–e). The states near the Fermi level were mainly occupied by O-2p states, which confirmed that most charge compensation was associated with oxygen redox. Generally, the electronic structures of the coated systems were similar to that of uncoated LiMnO$_2$. However, some impurity states, mainly occupied by C-2p states, were observed near the Fermi level in the coated systems, as shown in the magnified insets of Fig. 4(a–e). Therefore, the electronic conductivity should be increased to some extent upon coating with defective graphene, which should increase the rate capability of Li-rich cathode materials.

The (010) facet is the active plane for Li ion diffusion as the Li ions migrate most easily perpendicular to the (010) facet [22,29]. Hence, Li ion diffusion through the thickness of the coating layer is important for the rate capability of the coated cathode as the diffusion time (t) is determined by $t = L^2/D$, where $L$ is the diffusion length and $D$ is the diffusion coefficient. Therefore, Li ion diffusion through the pristine-/defective-graphene layer in the coated systems was studied using NEB methods. The energy profiles for Li ion diffusion are shown in Fig. 4(f–i). The activation barrier for Li ions penetrating the carbon ring of the pristine-graphene-coated system was 9.88 eV, which is similar to previously reported values of 9.7–10.2 eV for Li ion diffusion through pristine graphene [44–46], suggesting that Li ions cannot diffuse through such a coating. However, we observed that the presence of defects greatly decreased the energy barrier for Li ion diffusion; in the case of V4-type and V6-type defects, the barrier dropped to 1.44 and 0.16 eV, respectively. Therefore, the rate capability of defective-graphene-coated Li$_2$MnO$_3$ is expected to be substantially higher than in the case of pristine-graphene-coated samples. In addition, the reduced oxygen loss and Mn migration induced by the defective graphene coating should effectively avoid surface densification. As surface densification impedes Li$^+$ migration, we conclude that defective-graphene coatings increase Li ion diffusivity through the surface region of the host materials, which is expected to enhance the rate capability.

2.5. Experimental verification of the role of defective graphene

The theoretical calculations predicted that defective graphene can control the surface thermodynamic stability of Li$_2$MnO$_3$, which is expected to enhance the electrochemical performance of Li-rich cathode materials. These predictions were verified experimentally. A Li-rich Mn-based cathode (Li$_{1.2}$Ni$_{1.1}$Co$_{0.13}$Mn$_{0.54}$O$_2$) coated with defective graphene showed superior electrochemical performance, exhibiting a lower voltage degradation of only 0.35 V after 100 cycles under 2.0–4.8 V vs. Li anode at a 1 C rate compared to the values of 0.53 and 0.68 V for the pristine-graphene-coated and uncoated cases, respectively. The normalized capacity discharge profiles are shown in Fig. 5. The same trend was also observed when cycled versus Li over the voltage range of 2.0–4.6 V, where the voltage drops were 0.61, 0.47, and 0.08 V after 100 cycles at a 1 C rate for the uncoated, pristine-graphene-coated, and defective-graphene-coated samples, respectively. Thus, we conclude that the voltage decay was substantially reduced after graphene coating, which is consistent with our theoretical predictions.

As is shown in Fig. S10(a, b), the defective-graphene-coated sample exhibits the best cycling performance among the three samples, whose capacity retention is 93.5% after 100 cycles under 2.0–4.6 V at 1 C rate, higher than that of 84.4% and 79.8% for graphene-coated and uncoated sample, respectively. It is also true when cycled versus Li over the voltage range of 2.0–4.8 V, where the capacity retention is 89.7%,
82.3%, and 78.2% for defective-graphene-coated, graphene-coated, and uncoated samples, respectively. This confirmed the computational prediction of the enhanced stability.

The rate capability of the uncoated, graphene-coated, and defective-graphene-coated Li-rich materials was compared in Fig. S11(a, b). The rate capability is enhanced by graphene coating and defective-graphene coating, regardless of the voltage range of 2.0–4.6 V or 2.0–4.8 V. Furthermore, the rate capability of defective-graphene-coated samples is higher than that of pristine-graphene-coated samples, which is in accordance with the prediction of DFT calculation.

3. Conclusion

We investigated the use of a defective graphene coating to increase the surface thermodynamic stability of Li2MnO3. By controlling the size of the defect pore, we found that twofold-coordinated unsaturated carbon atoms in the V6-type defective graphene strengthened the interaction between the coating layer and host material, resulting in more stable binding compared to the other cases. The pores in the defective graphene structure can facilitate Li+ ion diffusion through the coating, resulting in faster diffusion compared to the pristine graphene case. The rate capability should considerably increase after coating with defective graphene due to further reduction of surface densification.

We showed that the defective graphene coating prevents oxygen release due to variations in the potential energy surface. To the best of our knowledge, this is the first report that reveals the critical role of potential energy surface in suppressing oxygen loss in Li-rich materials. These findings provide a deep understanding of the appropriate conditions for oxygen release from the surface, highlighting the limitations with respect to the potential energy surfaces around surface oxygen ions. Hence, it was possible to simultaneously maintain the degree of oxygen redox (to ensure high capacity values), while increase surface oxygen stability. We confirmed that Mn migration is coupled with oxygen loss, thus Mn migration was also suppressed by the defective graphene coating. The cycling stability should be enhanced by defective graphene coating. The main predictions of the theoretical study were confirmed by experimental results.

4. Experimental section

4.1. Computational details

All first-principles calculations presented here were performed using the Vienna ab initio simulation package (VASP) 5.4.4 [47], within the framework of density functional theory (DFT). The projector augmented wave method [48] with an energy cutoff of 550 eV was used to expand the wave functions. The exchange-correlation functional was described using the spin-polarized generalized gradient approximation (GGA) within the Perdew and Wang (PW91) formalism [49]. Furthermore, the strong correlation effect of the 3d state of the transition metal was taken into account using the GGA+U method [50] with a Hubbard U value of 4.5 eV for Mn ions, according to references [51,52]. In addition, van der Waals interactions were included in the calculations.

The Li2MnO3 surface was modeled by a symmetric periodic slab with a vacuum layer separation larger than 14 Å in all cases. A 2 × 2 supercell of Li2MnO3 (010)-slab with fifteen atomic layers contained 40 Li2MnO3 formula units (80 Li atoms, 40 Mn atoms, and 120 O atoms). The Monkhorst-Pack scheme [53] with 2 × 2 × 1 and 3 × 3 × 1 k-point meshes in the irreducible Brillouin zone was used for the structure optimization and calculation of the electronic properties, respectively. The total energies were converged to within 10−5 eV per formula unit. The lattice and ionic positions were both relaxed. The final forces on all atoms were less than 0.01 eV Å−1. The final distances in relaxed coated Li2MnO3 systems are 3.4–3.8 Å. As for the fully delithiated states, the final distances in relaxed coated MnO3 systems are 3.0–3.4 Å. The calculation of the density of states (DOS) was smeared using the Gaussian smearing method with a smearing width of 0.05 eV. The Li diffusion paths and energy barriers were obtained using the nudged elastic band (NEB) method [54,55].

4.2. Sample preparation

The Li1.2Ni0.15Co0.15Mn0.53O2 sample was synthesized via a sol-gel method to obtain the precursor. Stoichiometric amounts of lithium acetate dihydrate (5% excess), nickel acetate tetrahydrate, manganese acetate tetrahydrate, and cobalt acetate tetrahydrate were mixed and dissolved in deionized water with citric acid as the complexing agent and ethylene glycol as the dispersant. The sol was evaporated using a rotary evaporator leading to the formation of a hydrous gel. The hydrous gel was then dried at 150 °C for 8 h. Then, the dried gel was milled with a mortar and a pestle. Finally, the samples were sintered at 450 °C for 4 h and then at 900 °C for 15 h to produce the target products. In order to apply the pristine/defective graphene coatings, pristine or defective graphene (the mass ratio of pristine/defective graphene and the Li-rich Mn-based material is 1: 5) was added to the products with an assisting solvent of tert-butanol to redisperse pristine/defective graphene and simultaneously avoid water damage to the hydrophobic. After the mixture was processed by ultrasonics, the composite was dried at 100 °C in vacuum oven overnight. In addition, the graphene and defective graphene was obtained from reduction of graphene oxide (J & K, CAS: 1034343-98-0) and defective graphene oxide by hydrazine treatment, respectively (details was described in Supporting information).

Defective graphene oxide was synthesized according the Ruoff’s method [56]. The pore size of the defective graphene was about 0.6–5 nm. The annular dark field scanning transmission electron microscopy (ADF-STEM) image of our obtained defective graphene sample is shown in Fig. S12. As can be seen clearly in Fig. S12(b), many defects with pore size less than 1 nm (outlined as red circles) has been generated. Meanwhile, the defects with pore size up to 5 nm (outlined as blue circles) has also been generated, which agrees well with the reference [56]. Moreover, small fraction of edge atoms of the obtained defective graphene was proved by EPR signal in the reference [56], thus have little driving force to trap oxygen. The cathode electrodes were prepared via mixing 90 wt % active materials, 5 wt % Polyvinylidene Fluoride (PVDF) as the binder, and 5 wt % Super P as the conductive additive.

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Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ensm.2019.01.004.

References
