Enhanced Li-O₂ battery performance, using graphene-like nori-derived carbon as the cathode and adding LiI in the electrolyte as a promoter

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Abstract

To rapidly promote the development of electric vehicles, an efficient cathode catalyst for Li-O₂ batteries is urgently needed. In the present study, we prepared a new type of doped carbon catalyst derived from nori biomass for the cathode of Li-O₂ batteries, using a hydrothermal carbonization and pyrolysis method. The catalyst presented a graphene-like nanosheet structure, a high surface area, and excellent ORR/OER activity. Li-O₂ batteries with this catalyst exhibited superior round-trip efficiency (at current densities of 500 mA/g, the corresponding coulombic efficiency was 99.8%) and excellent cycling stability (100 stable cycles at 200 mA/g under capacity limitation). Furthermore, the charge–discharge overpotential could be reduced dramatically by adding LiI to the electrolyte, resulting in greatly enhanced battery performance. The battery's energy efficiency was over 90%, even after 100 cycles at limited capacity. We concluded the following: (i) the high surface area and

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nanosheet structure of the nori catalyst provided sufficient space not only to accommodate the discharge products but also to guarantee that oxygen, soluble catalyst, and lithium ions could be freely transported; and (ii) these combined with the redox mediator LiI that was added to the electrolyte, which could freely access the interior of the air electrode, easily reacting with the solid discharge products and effectively changing the morphology and chemical nature of the discharge products. We believe these factors were responsible for the significantly enhanced performance of the resulting Li-O₂ batteries, suggesting this method may be a facile way to achieve a high-performance Li-O₂ battery.

Keywords: Li-O₂ battery; Biomass-derived; Nori; Doped carbon catalyst; Cathode catalyst

1. Introduction

The rapid development of electric vehicles (EVs) is a focus of intense worldwide interest due to concerns about energy shortages and environmental deterioration. However, such development is highly dependent upon energy storage devices, as these determine the driving range and practical applications of EVs. To meet these demands, Li-O₂ batteries—which have twice the theoretical energy density of current Li-ion batteries—have attracted a great deal of attention as one of the most promising power sources for EVs [1, 2]. Some exciting research progress has been achieved in recent years [3-5], but key limitations remain, such as the sluggish kinetics of the oxygen reduction reaction (ORR) during the discharge process, and the oxygen

evolution reaction (OER) during the charge process, which lead to large discharge–charge overpotential, poor rate capability, poor reversibility, and short cycle life [6, 7]. Thus, an efficient cathode catalyst to accelerate the kinetics is urgently needed.

Doped carbon materials have been widely investigated for Li-ion batteries [8], supercapacitors [9], and fuel cells [10], due to their low cost, porous morphology, and much higher ORR activity in comparison with conventional carbon materials. They have exhibited excellent cathodic performance in Li-oxygen batteries [11], and their high surface area and porous structure not only can accommodate solid discharge products but also can ensure oxygen diffusion and electrolyte impregnation [12]. Li et al. introduced N-CNTs as cathode materials for Li-O₂ batteries, showing that nitrogen doping increased discharge capacity and enhanced reversibility [13]. They also reported that sulphur-doped graphene could significantly influence battery performance and the morphology of discharge products [14]. Previously, our group demonstrated that multi-element co-doped graphene presented ultra-high ORR activity in comparison with a commercial Pt/C catalyst, in both aqueous and non-aqueous electrolytes [15]. Clearly, doped carbon materials may be promising as cathode catalysts for high-performance Li-O₂ batteries.

Biomass is an ideal precursor for preparing doped carbon material: it is inexpensive, it has a porous structure, structural variety, and a high surface area, and it is rich in multiple elements. Indeed, biomass materials have been widely investigated for use in supercapacitors [16] and fuel cells [17]. It is therefore reasonable to expect

that doped carbon catalysts for high-performance Li-O₂ batteries could be prepared using biomass precursors. To date, however, only one study has reported the creation of a biomass-derived carbon catalyst for use in Li-O₂ batteries. Xia et al. synthesized mesoporous carbon nanofiber arrays using a natural crab shell template coated with RuO₂ as a catalyst, and the resulting Li-O₂ battery had high capacity and a long cycle life [18]. Nevertheless, no studies have been published on preparing doped carbon materials from botanic biomass to use as the cathode catalyst for Li-O₂ batteries.

Previous reports have demonstrated that the OER activity of doped carbon catalysts is insufficient for high-performance Li-O₂ batteries [19, 20]. Tremendous efforts have been made to form composite catalysts that combine carbon materials with those that have high OER activity (such as noble metals [21], transition metals [22], and their oxides [23]). The composite catalysts thus far reported have exhibited distinctly enhanced performance in Li-O₂ batteries. Recently, the use of a soluble catalyst was presented as a new strategy to dramatically enhance battery performance, with LiI being demonstrated as an effective candidate [3, 24].

Nori—a marine algae biomass that has a special thin-film structure and is rich in multiple elements—has been chosen as the precursor for preparing a doped carbon catalyst using a hydrothermal carbonization and pyrolysis method by our group previously [25], and the catalyst demonstrated outstanding ORR performance. As a continuous work, we attempted to use this catalyst as cathode of Li-O₂ battery, interestingly; it exhibited excellent ORR/OER activity, superior round-trip efficiency and excellent cycling stability. At current densities of 500 mA/g, the battery delivered

a coulombic efficiency of 99.8%. The battery also achieved 100 stable cycles under a limited capacity of 600 mAh/g. Once we added LiI as a redox mediator in combination with our nori catalyst, the battery's charge–discharge overpotential dropped significantly, resulting in dramatically enhanced performance: the battery's energy efficiency was over 90% after 100 cycles at a limited capacity of 1000 mAh/g.

2. Experimental

Materials synthesis

The nori was purchased from a supermarket. Before use, the nori was rinsed with deionized water, dried at 80°C overnight, then ground into powder. We prepared the doped carbon catalyst derived from nori biomass as follows. First, 2 g nori powder and 2 g melamine were dispersed with 40 mL deionized water and stirred for 2 h. Next, the mixture was added to a Teflon-lined steel autoclave and heated to 190°C for 8 h, as previously reported by our group [25]. Then, the product was dried overnight in a vacuum at 80°C and fully ground into a fine power. This powder was pyrolyzed at 1000°C for 1 h in an Ar flow, then leached in 1.0 M H₂SO₄ at 80°C for 6 h. Finally, the sample was annealed at 1000°C in an Ar atmosphere for 30 min, then in an ammonia flow for 30 min. We call the final product NORI.

For comparison, we also prepared Li-O₂ batteries with cathodes of (a) XC-72R carbon black (Cabot, US), (b) Super P carbon black (SP, Timcal), and (c) reduced graphene oxide (rGO, prepared by a modified Hummer's method with a simple thermal expansion approach).

Material characterization

X-ray powder diffraction (XRD) was carried out on a TD-3500 powder diffractometer (Tongda, China) operated at 40 kV and 30 mA, using Cu-K α radiation sources. X-ray photoelectron spectroscopy (XPS) was conducted on an ESCALAB 250 X-ray photoelectron spectrometer (Thermo-VG Scientific, USA). Scanning electron microscopy (SEM) was recorded on a Nova Nano 430 field emission scanning electron microscope (FEI, USA). Transmission electron microscopy (TEM) was conducted with a JEM-2100HR transmission electron microscope (JEOL, Japan).

Electrochemical testing

Electrochemical tests were conducted in 2032-type coin cells with holes made in the cathode to permit oxygen flow. The cathode electrode was prepared as follows. We mixed the prepared catalyst (NORI or one of the other materials, 90 wt%) with polyvinylidene fluoride (PVDF, 10 wt%) binder in N-methyl-2-pyrrolidone (NMP) to form a slurry. We then coated the catalyst slurry on carbon paper and dried it at 80°C overnight in a vacuum oven.

The Li-O₂ cell was assembled in an Ar-filled glove box (Etelux LAB2000) with O₂ and H₂O < 0.1 ppm. Lithium foil 16 mm in diameter was used as the anode, and a polypropylene (Celgard 2400) membrane was used as the separator. 1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in tetraethylene glycol dimethyl ether (TEGDME) was the electrolyte, and 0.5 M LiI was the redox mediator dissolved into the electrolyte. The refined and purified TEGDME electrolyte was provided by a professional Chinese company, the water content is lower than 20 ppm.

All the Li-O₂ cells were operated in a pure oxygen atmosphere within a sealed glass bottle and were tested with a battery testing system (Neware, CT-3008, China) at room temperature. Before the test, the cell was rested for 5 h in an oxygen atmosphere. The specific capacities and current density were calculated using the total weight of the carbon materials.

3. Results and discussion

Structural characterization

Fig. 1 presents the XRD patterns and nitrogen adsorption–desorption isotherms of the XC-72R and NORI materials. As Fig. 1 (a) demonstrates, the nori-derived doped carbon catalyst exhibited almost the same XRD patterns as the XC-72R carbon black; they had nearly the same C (002) and C (101) diffraction peaks and peak intensities, suggesting that our NORI catalyst would have a good degree of graphitization.

As Fig. 1 (b) shows, the NORI catalyst exhibited quite different isotherms from those of the XC-72R. The former presented a Type I isotherm with a distinct hysteresis loop in the region of $P/P_0 = 0.5-1$, indicating that the NORI catalyst may have had both microporous and mesoporous structures. The XC-72R showed a Type II isotherm, with higher adsorption at high pressures. The BET surface areas of the NORI and XC-72R were 738 and 189 m²/g, respectively. The NORI's high specific surface area, along with its microporous and mesoporous structure, are promising for oxygen transport, could provide more space to accommodate discharge products, and

could lead to high performance in Li-O₂ batteries.

Fig. 1 (c) presents the XPS survey spectra of the NORI catalyst, showing a dominant C 1s peak, a N 1s peak, an O 1s peak, and S 2p peaks. The catalyst surface composition data also shown in this figure are derived from these spectra. The NORI catalyst had a high N content (5.11 at%) and a high S content (0.76 at%), most likely due to the nitrogen doping process and the composition of the nori.

Fig. 1 (d) presents the deconvolution results of the N 1s peak for the NORI catalyst. It is known that pyridinic N (398.4 eV), pyrrolic N (399.8 eV), and graphitic N are active species in a doped carbon catalyst. Based on the deconvolution data, our NORI catalyst clearly had high active N content (4.71 at%), which may have been the main reason for its much higher ORR performance. It is well known that nori is rich in iodine, yet we detected only a trace of iodine (0.02 at%) in the NORI catalyst, which was too little to investigate its role in the catalyst's activity.

Morphological characterization

Fig. 2 (a-d) shows SEM and TEM images of the NORI catalyst. A thin, graphene-like nanosheet structure is evident, the nanosheets loosely overlapping and stacking and thereby easily forming a porous structure. Our previous work [25] suggested that this unique structure is attributable to the thin-film morphology of nori biomass. The high specific surface area of 738 m²/g also confirms the catalyst's porous, graphene-like nanosheet structure. HRTEM images of the NORI catalyst (Fig. 2 (d)) clearly reveal the porous structure, which is consistent with the nitrogen adsorption-desorption results. Further, the EDS results (Fig. 2 (e)) also evidence the

existence of nitrogen, sulfur, and iodine, consistent with the XPS result. We could expect that this catalyst's high surface area, porosity, and graphene-like nanosheets would result in high performance in a Li-O₂ battery.

Electrochemical characterization

Fig. 3 compares the electrochemical impedance spectra and CV curves for Li-O₂ batteries with either NORI or XC-72R as the cathode catalyst. The two EIS curves in Fig. 3(a) are similar in shape, both presenting a semicircle and a linear tail. The corresponding equivalent circuit is inside the figure. Evidently, the charge transfer resistance (*R*_{ct}) of the XC-72R cathode (88.37 ohm) was much higher than that of the NORI cathode (64.31 ohm), revealing the latter's enhanced ionic conduction path, which may have resulted in the higher performance of the corresponding Li-O₂ batteries (Table. S1) [26].

Fig. 3 (b) presents the electrocatalytic activity of the NORI and XC-72R cathodes with in situ cyclic voltammetry (CV). The ORR onset potential of the NORI cathode was 2.92 V higher than that of the XC-72R cathode (2.8 V), indicating lower ORR kinetic polarization and better ORR activity. During the anodic scan section, the current density for the NORI cathode was greater and the discharge product decomposition voltage was lower, clearly pointing to the superior OER activity of the NORI catalyst. This result was also supported by the later discharge-charge profiles.

Fig. 4 (a) compares the initial discharge-charge profiles of Li-O₂ batteries with various cathodes in the range of 2.2–4.4 V. Notably, the NORI cathode exhibited a high discharge capacity of 4222 mAh/g at a current density of 200 mA/g, which was

larger than the values for the XC-72R cathode (1743 mAh/g), the SP cathode (2199 mAh/g), and certain previously reported noble metal cathodes [27], and comparable to the discharge capacity of a rGO cathode (4702 mAh/g) with a similar structure. Clearly, the nori-derived, doped carbon catalyst exhibited good ORR and OER activity, unlike most doped carbon catalysts (which have good ORR activity but poor OER activity [13, 28]).

More important was that the NORI cathode had superior rate capability. At a current density of 500 mA/g, the battery with the NORI cathode delivered a capacity of 3196 mAh/g, and the corresponding coulombic efficiency was 99.8%, suggesting that the catalytic activity of NORI was superior to that of other composite catalysts in terms of round-trip efficiency [29]. For current densities up to 1000 mA/g, the capacity of the NORI cathode (1324 mAh/g) was almost 7.5 times higher than that of the XC-72R cathode (176 mAh/g, Fig. S2), indicating the former's excellent rate capability.

To further understand the cycling stability of the NORI catalyst as the cathode in a Li-O₂ battery, we applied galvanostatic cycling at 200 mA/g with a cutoff capacity of 600 mAh/g. As shown in Fig. 4 (d), the battery with the NORI cathode achieved 100 stable cycles while the discharge terminal voltage remained above 2.0 V, and in the first cycle, the energy efficiency reached 75.1%, indicating excellent stability during the ORR. During the initial 10 cycles, the charge plateau remained below 4.0 V, further demonstrating the NORI catalyst's enhanced OER activity. In contrast, the XC-72R, SP, and rGO cathodes (Fig. S3) achieved only 23, 16, and 21 stable cycles,

respectively, and their energy efficiency decreased sharply after 20 cycles. Compared with previously reported carbon [30] or metal composite catalysts [31, 32], the NORI cathode demonstrated superior cycling stability.

Why was this nori-derived doped carbon catalyst so effective? We suggest the following possible explanations: (a) the novel biomass feedstock and preparation method led to the doped carbon catalyst having high ORR and OER activity, facilitating both discharge and charge processes; (b) the high surface area and unique, graphene-like nanosheet structure provided sufficient oxygen diffusion pathways, more three-phase interfaces, and enough space to accommodate the discharge products.

However, we also found that the charge plateau began to increase after the 10th cycle with the NORI cathode—possibly because of the limited OER activity—which led to high charge voltage and battery performance degradation. Previous reports have demonstrated that the OER activity of doped carbon catalysts is insufficient for high-performance Li-O₂ batteries [19, 20].

Recent reports have revealed that adding a soluble catalyst to the electrolyte can dramatically enhance a battery's performance [33]. We therefore added LiI to gauge its effect.

Fig. 5 shows the electrochemical performance of Li-O₂ batteries with the addition of LiI. The performance was dramatically enhanced. Compared with Fig. 4 (c) and 4 (d), the charge–discharge overpotential of both XC-72R electrode and NORI electrode dropped significantly with the addition of LiI, suggesting that the insulating

discharge products were the main cause of the polarization. Obviously, the overpotential decrease caused by the addition of LiI with the NORI electrode is far more than that caused by the addition of LiI with the XC-72R electrode.

As shown in Fig. 5 (b), the Li-O₂ battery with NORI+LiI performed at least 100 stable cycles with no loss of specific capacity and no significant change in the discharge–charge curves, indicating the superior reversibility of this cathode. The energy efficiency reached 91.32% in the first cycle and 96.25% in the second cycle and remained over 90% at 100 cycles. In comparison, the battery with XC-72R+LiI reached 85.38% in the first cycle and 91.35% in the second cycle, then sharply decreased to 77.35% after 20 cycles.

Encouraged by the excellent cycling stability of NORI+LiI, we further examined its capacity and rate capability. With the addition of LiI, the discharge capacity at a rate of 200 mA/g reached 10430 mAh/g—almost 2.5 times that of the battery without the addition of LiI. The former also exhibited very high rate capability; even at current densities of 500 and 1000 mA/g, the batteries yielded discharge capacities of 5182 and 3026 mAh/g, and the coulombic efficiency remained near 100%. All of these values are much higher than those for the battery without LiI, clearly revealing LiI's significant role.

The dramatically improved electrochemical performance of the Li-O₂ battery after the addition of LiI can be attributed to the synergistic effect between LiI and the unique structure of our NORI cathode. The LiI functioned as a moveable ion catalyst and a redox mediator, freely accessing the interior of the air electrode and easily

reacting with the solid discharge products, thereby significantly reducing the overpotential. The NORI catalyst had a high surface area and a unique graphene-like nanosheet structure, which provided sufficient space not only to accommodate the discharge products but also to guarantee the free transportation of the oxygen, soluble catalyst, and lithium ions. These results were consistent with previous reports [34].

To further investigate the reversibility of Li-O₂ batteries with NORI and NORI+LiI cathodes, we used EIS and XRD. As shown in Fig. 6 (a, b), the battery's charge transfer resistance with both cathodes increased significantly after discharge to 2.2 V at a current density of 200 mA/g, and decreased almost to the initial value after charge. Through simulation using an equivalent circuit, the ohmic resistance (R_s) and charge transfer resistance (R_{ct}) of the Li-O₂ batteries with the NORI and NORI+LiI electrodes were calculated and are listed in Table S2. It is interesting that the Li-O₂ batteries with NORI and NORI+LiI exhibited similar initial ohmic resistance, but the latter exhibited much lower charge transfer resistance.

EIS results revealed the significant promotion effect of LiI. In the NORI cathode battery without added LiI, the R_{ct} increased significantly, from 64.31 to 174.5 ohm after discharge, then dropped to 76.1 ohm when the cell was charged, indicating the significant effect of the insulating discharge products on the charge transfer resistance. However, for the battery with the NORI cathode and added LiI, the increase in R_{ct} was much less after the battery was discharged (from 40.86 to 62.86 ohm), and it recovered to almost the initial value after charging (51.49 ohm), clearly revealing that the addition of LiI improved the ionic conduction pathways and kinetics of the

ORR/OER.

Fig. 6 (c) shows the XRD clearly indicates the main discharge product on the NORI cathode was Li_2O_2 , which almost fully disappeared when the battery recharged to 4.4 V, confirming the good reversibility of the NORI cathode. As shown in Fig. 6 (d), after discharge to 2.2 V, all peaks can be indexed to LiOH , indicate that LiOH was the only observed discharge product when LiI was added. When the cell was charged, LiOH was fully disappeared, which agrees with previous results [34].

Fig. 7 (a, b) shows that the discharge products from the NORI electrode were massive nanospheres and nanoplates of Li_2O_2 [35]; these were confirmed by XRD analysis (Fig. 6 (c)). The small and well-dispersed Li_2O_2 nanoparticles would have been much more easily decomposed than the larger aggregates of Li_2O_2 , which may explain the high capacity and excellent cycling stability of the battery with the NORI cathode.

Interestingly, in the case of the battery with LiI , the morphologies of the discharge products were significantly different from those formed on the NORI cathode without LiI . The discharge products from the former exhibited a porous and petal-shaped morphology, consisting of massive nanosheets (Fig. 7 (c, d)). The XRD results also showed that LiOH —but not Li_2O_2 —was one of the main discharge products (Fig. 6 (d)) when LiI was added, which is consistent with previously reported results [34, 36]. Liu et al. have pointed out that the dominant H^+ source for LiOH is water from the surroundings rather than from the electrolyte [34]. Clearly, the addition of LiI changed not only the morphology and structure of the discharge

products but also their chemical state—or else it changed the mechanism of the reaction that occurred on the cathode.

In summary, we suggest that the promotion of LiI could be explained by the following: (a) It changed the morphology and structure of the discharge products. The unique, porous, petal-like morphology of the discharge products provided more channels for oxygen molecules to diffuse and sufficient interfaces for the cathode reaction; (b) it acted as a moveable catalyst and a redox mediator, changing the mechanism of the cathode reactions during the charging and discharging processes and thereby resulting in different discharging products. LiI may have facilitated the reduction and evolution of oxygen at the cathode of the Li-O₂ battery.

4. Conclusion

We prepared a doped carbon catalyst with nori biomass as the precursor (NORI), then used it as the cathode in a lithium oxygen battery. This NORI presented a graphene-like nanosheet structure, high surface area, and good ORR/OER activity. Li-O₂ batteries with the NORI cathode exhibited superior round-trip efficiency and excellent cycling stability. Interestingly, adding LiI to the electrolyte as a soluble catalyst dramatically enhanced the performance of the Li-O₂ batteries, yielding an energy efficiency of over 90% even after 100 cycles of limited capacity at 1000 mAh/g. The discharge products were also different in the absence of LiI. This work may provide a new strategy for preparing high-performance Li-O₂ batteries.

Acknowledgments

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Captions for Figures

Fig. 1 (a) XRD patterns and (b) nitrogen adsorption–desorption isotherms of XC-72R and NORI materials. (c) XPS survey spectrum, (d) N 1s spectra of NORI material.

Fig. 2 The NORI catalyst: (a, b) SEM images; (c, d) TEM images; (e) the corresponding EDS spectrum.

Fig. 3 (a) Electrochemical impedance spectra of Li–O₂ batteries with different catalysts; (b) in situ CV curves of Li–O₂ batteries with different catalysts.

Fig. 4 (a) The initial discharge–charge profiles of Li–O₂ batteries with different

cathode catalysts. (b) The discharge–charge profiles of the NORI cathode at various current densities. The discharge–charge cycles of Li-O₂ cells with (c) XC-72R and (d) the NORI cathode at 200 mA/g with a curtailing capacity of 600 mAh/g. (e) The specific energy efficiency at different cycles with various cathodes.

Fig. 5 (a) The initial discharge–charge profiles of Li-O₂ batteries with XC-72R+LiI and NORI+LiI at 500 mA/g, with a curtailing capacity of 1000 mAh/g. (b) The discharge–charge cycles of Li-O₂ cells with NORI+LiI at 500 mA/g with a curtailing capacity of 1000 mAh/g. (c) The corresponding specific energy efficiency at different cycles with different cathodes. (d) The initial discharge–charge profiles of Li-O₂ batteries with NORI+LiI at various discharge current densities.

Fig. 6 Electrochemical impedance spectroscopy spectra (a, b) and XRD patterns (c, d) of the Li-O₂ cell with different cathode catalysts at different cycles.

Fig. 7 SEM images of the Li-O₂ cells with different cathode catalysts after discharge to 2.2 V at 200 mA g⁻¹: (a, b) NORI; (c, d) NORI+LiI.

Fig.1

Fig.2

Fig.3

Fig.4

Fig.5

Fig.6

Fig.7

Graphical Abstract