Doped reduced graphene oxide mounted with IrO₂ nanoparticles shows significantly enhanced performance as a cathode catalyst for Li-O₂ batteries

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Abstract

In this work, a high-performance composite catalyst comprised of IrO₂ nanoparticles mounted on Co and N co-doped reduced graphene oxide (Co-N-rGO) is designed and successfully prepared for use in a Li-O₂ battery. A battery with this catalyst as the cathode demonstrates very high capacity retention ability and cycling stability: it delivered a high reversible capacity of 11,731 mAh g⁻¹ after five cycles at 200 mA g⁻¹, and after 200 cycles with limited capacity of 600 mAh g⁻¹, the battery's discharge terminal voltage remains over 2 V and its energy efficiency still above 65%. Doping with Co and N, along with mounting the IrO₂ nanoparticles, greatly enhances the catalyst's performance. We suggest that its outstanding performance is attributable to the high surface area of rGO, the enhanced oxygen reduction reaction (ORR) activity arising from doping with Co and N, and the high dispersion and great promotion of IrO₂ nanoparticles.

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1. Introduction

The rechargeable Li-O₂ battery has many advantages over other batteries that are currently in common and widespread use. In particular, its ultra-high theoretical energy density makes it a promising alternative power source for electric vehicles, as this feature would solve the presently intractable mileage limitation problem in today's electric vehicles. However, several critical problems must be resolved, the most significant being the lack of an efficient cathode, which leads to sluggish kinetics in the cathodic reactions [1, 2].

Overcoming this problem requires an efficient catalyst for both the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER). Various carbon materials have been proposed [3-5], among which graphene-based catalysts have proven to be the best, due to their outstanding electrical conductivity and large surface area [6-9]. Xiao et al. designed hierarchically porous graphene as the air electrode for a Li-O₂ battery and achieved exceptionally high discharge capacity [10]. Li et al. demonstrated that a Li-O₂ battery with a nitrogen-doped graphene catalyst delivered a 40% higher discharge capacity than one using pristine graphene [11]. Some researchers have used graphene as a support material on which to load metals and metal oxides, creating composite catalysts. Sun et al. reported that a graphene and Co₃O₄ nanocomposite showed efficient ORR/OER activities for aqueous Li-O₂ batteries [12]. Our group recently presented graphene co-doped with multielements and mounted with Ru nanoparticles as an ultra-high-efficiency cathode catalyst for the ORR/OER [13].

1 In most situations, pure carbon materials have poor OER activity, so creating
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3 composite catalysts by introducing suitable OER catalysts into graphene can be quite
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5 effective [14-16]. IrO₂, recognized as the best catalyst for the OER, is widely used for
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7 fuel cell and water electrolysis [17, 18] but seldom employed in Li-O₂ batteries. Yet
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9 Manthiram et al. reported that nanocrystalline IrO₂ exhibited much better OER
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11 activity than a Pt/C catalyst [19]. Guo et al. demonstrated that IrO₂/KB electrode
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13 exhibits remarkable catalytic activity towards OER, and Li-O₂ battery with this
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15 electrode can maintain a long cycle life for 70 cycles under a limited capacity of 500
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17 mAh g⁻¹ [20]. The ORR activity of IrO₂ and the dispersion of IrO₂ nanoparticles are
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19 problematic, but we can use a carbon material to make up for this deficiency, and
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21 graphene is ideal.
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31 Herein, we use a facile method to prepare graphene co-doped with Co and N,
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33 which become the carbon matrix for supporting IrO₂ nanoparticles to create a new
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35 catalyst for Li-O₂ batteries. The Li-O₂ battery with this catalyst as cathode displays
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37 excellent capacity retention ability and outstanding cycling stability: it delivered a
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39 high reversible capacity of 11,731 mAh g⁻¹ after five cycles at 200 mA g⁻¹, and after
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41 200 cycles with limited capacity of 600 mAh g⁻¹, the terminal voltage remains above
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43 2 V and the energy efficiency still above 65%. To our knowledge, this is the first time
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45 anyone has designed and prepared doped rGO mounted with IrO₂ nanoparticles for
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47 use in non-aqueous Li-O₂ batteries.
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56 The schematic diagram shown in Fig 1 presents the possible structure of the
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58 catalyst and the possible mechanism for the promotion of IrO₂.
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2. Experimental

2.1 Materials synthesis

We prepared the rGO co-doped with Co and N (Co-N-rGO) using a high-temperature doping process previously reported by our group [13]. The mass ratio of rGO, melamine, and Co was 1:5:0.05. A typical preparation process can be described as follows: 200 mg rGO was dispersed in 10 mL ethanol and sonicated for 1 h, then desired amount of $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (as the Co precursor) and melamine (as the N precursor) were added and stirred constantly for 10 h, then the solvent was removed by evaporating, and the mixture was annealed at 850 °C for 30 min in an Ar atmosphere. The product was further leached in 1.0 M H_2SO_4 at 80 °C for 6 h, and followed by annealing at 850 °C for 30 min in an Ar atmosphere. The resulting samples are denoted as Co-N-rGO.

The IrO_2 nanoparticles were prepared and mounted on Co-N-rGO by a facile hydrothermal method. 0.1 g Co-N-rGO was impregnated with 5.24 mL IrCl_3 solution (5.67×10^{-2} M), then sonicated for 2 h and stirred for 12 h. Next, the mixture was transferred to an autoclave with a 100 mL Teflon liner and reacted at 180°C for 12 h, then washed with deionized water and dried in a vacuum at 80°C for 12 h. We denoted the final catalyst as $\text{IrO}_2/\text{Co-N-rGO}$. Inductively coupled plasma-atomic emission spectrometry (ICP-AES) analysis results indicated the Ir content of the prepared catalysts to be 28.29 wt.%.

2.2 Material characterization

The catalysts were characterized by X-ray powder diffraction (XRD, Tongda

TD-3500 powder diffractometer), scanning electron microscopy (SEM, FEI Nova Nano 430), transmission electron microscopy (TEM, JEOL JEM-2100HR), X-ray photoelectron spectroscopy (XPS, ESCALAB 250), elemental analysis (EA, Elementar GmbH), and ICP-AES (Leema PROFILE).

2.3 Electrochemical testing

Electrochemical tests were conducted using a 2032-type coin cell with several holes in the cathode to let oxygen pass through. The cathode electrode was prepared by mixing the prepared material (90 wt.%) with polyvinylidene fluoride binder (PVDF, 10 wt.%) in N-methyl-2-pyrrolidone (NMP) to form a slurry. The slurry was then spread onto carbon paper and dried in a vacuum at 80°C overnight. The cell was assembled in an Ar-filled glove box (Etelux LAB2000). Lithium foil was used as the anode, and a polypropylene membrane (Celgard 2400) formed the separator. The electrolyte was 1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) dissolved in tetraethylene glycol dimethyl ether (TEGDME).

The cells were tested on a CT-3008 battery testing system (Neware, China) at room temperature. To avoid the effects of moisture, the testing cell was sealed in an oxygen-filled glass bottle containing a dryer. Galvanostatic discharge-charge cycling was performed using the cut-off capacity method, and the discharge capacity was then calculated using the total weight of the cathode catalyst (carbon+IrO₂). The loading of the catalyst on each electrode was 0.3-0.5 mg. Cyclic voltammetry (CV) was conducted on an electrochemical workstation (Ivium, the Netherlands), with scanning rate of 0.5 mV s⁻¹.

3. Results and discussion

3.1 Structure and morphology characterization

The catalysts' XRD patterns are shown in Fig. 2a. All the diffraction peaks fit well with the standard diffraction data for IrO₂ and the graphene (002) plane, but there are no peaks associated with Co. The results clearly confirm the existence of IrO₂, and the broad IrO₂ peak may indicate the presence of very small IrO₂ nanoparticles [20]. Fig. 2b presents the XPS survey spectra of IrO₂/Co-N-rGO and Co-N-rGO. The peaks of C 1s (~284.8 eV), O 1s (~532.0 eV), N 1s (~400.0 eV), and Co 2p (775-805 eV) in both spectra confirm the existence of Co and N in the doped rGO [21]. We also find the peaks for Ir 4p (~494.8 eV) and Ir 4f (60-70 eV) in the spectrum of IrO₂/Co-N-rGO [22]. Comparison of the two spectra shows that IrO₂/Co-N-rGO had a much higher O content (17.32 at.%) than Co-N-rGO (5.54 at.%), possibly due to the existence of iridium oxide.

Fig. 2c shows the deconvolution results of the N 1s spectrum of IrO₂/Co-N-rGO, according to the literature, the five deconvolution peaks correspond to pyridinic-N (398.4 eV), metallic-N (399.5 eV, Co-N), graphitic-N (401.3 eV), pyrrolic-N (400.3 eV), and oxidated-N (403.1 eV) [23], respectively. The total fraction of active N species (pyridinic, metallic, graphitic, and pyrrolic) in our catalyst reaches 84.4 at.% based on the integration results of each peak's area, which we would expect to result in high activity.

Fig. 2d shows the Ir 4f spectra of IrO₂/Co-N-rGO and the deconvolution results

1 of Ir $4f_{5/2}$ and Ir $4f_{7/2}$. The peaks at 65.2 and 62.2 eV correspond to the binding
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3 energies of $4f_{5/2}$ and $4f_{7/2}$ of Ir^{4+} , and the peaks at 66.1 eV and 63.1 eV correspond to
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5 the $4f_{5/2}$ and $4f_{7/2}$ of Ir^{x+} [22], which is a higher oxidation state Ir than Ir^{4+} . The
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7 calculated atomic fractions of Ir^{4+} and Ir^{x+} are 72 at% and 28 at%, confirming that Ir
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9 mainly existed as Ir (IV) in the doped catalyst.
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16 analysis. The Ir content of $\text{IrO}_2/\text{Co-N-rGO}$ was 28.29 wt.%, and the values for Co, N,
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18 and C were 1.12, 4.02, and 50.3 wt.%, respectively. In Co-N-rGO, the values for Co,
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20 N, and C were 1.51, 4.41, and 84.11 wt.%, respectively.
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25 The SEM and TEM images of $\text{IrO}_2/\text{Co-N-rGO}$ presented in Fig 3 show the
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27 typical morphology of graphene. The wrinkled, curled structures could easily form
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29 porous 3D networks and provide enough space for the deposition of discharge
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31 products; they could also facilitate the diffusion of oxygen to the catalyst, resulting in
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33 high performance [24]. The IrO_2 nanoparticles were homogeneously distributed on
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35 the surface of Co-N-rGO (Fig 3d), with an average particle diameter of about 1.61 nm.
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37 The HRTEM image shown in the insert of Fig 3d clear presents the well-defined
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39 crystalline lattice fringes of the nanoparticles, these fringes (0.258 nm) refer to the
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41 (101) facet of IrO_2 , revealing the mounting of IrO_2 nanoparticles on the doped
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53 Fig. 4 shows the STEM images and the corresponding elements EDX mapping
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55 images of Co-N-rGO and $\text{IrO}_2/\text{Co-N-rGO}$ catalysts. It can be seen that the N and Co
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57 signals were homogeneously distributed over the graphene surface, indicating the N
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1 and Co were successfully doped into the graphene. Fig. 4 (l) reveals the uniform
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3 dispersion of Ir on the surface of N and Co co-doped graphene.
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8 9 3.2 Electrochemical characterization

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11 Fig. 5a compares the electrochemical impedance spectra for Li-O₂ batteries with
12 the rGO, Co-N-rGO, or IrO₂/Co-N-rGO cathode. Fitting the spectra with the
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14 equivalent circuit shown in Fig 5a, we obtain the R_{ct} and R_s of the catalysts (Table 1),
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16 the co-doping of N and Co could significantly decrease the R_s of the rGO, but
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18 decrease the R_{ct} by 10%. Interestingly, the further mounting of IrO₂ nanoparticles
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20 almost cannot change the R_s of the materials, but obviously decrease the R_{ct} of the
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22 material. It implies that the mounting of IrO₂ nanoparticles great enhanced the
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24 electrochemical activity of the catalyst.
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34 Fig. 5b presents the in situ CV curves at 0.5 mV s⁻¹ in LiTFSI/TEGDME to
35 investigate the electrocatalytic activity of the rGO, Co-N-rGO, or IrO₂/Co-N-rGO
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37 cathode. Fig. 5b shows that both IrO₂/Co-N-rGO (-1.16 A/g) and Co-N-rGO (-0.79
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39 A/g) had one significant reduction peak and high ORR current density, which
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41 indicates better ORR activity than that of rGO (-0.21 A/g). In the anodic oxidation
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43 region, IrO₂/Co-N-rGO (1.04 A/g) showed much higher current density than
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45 Co-N-rGO (0.82 A/g) and rGO (0.26 A/g), with three strong oxidation peaks clearly
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47 indicating the enhanced OER activity of the composite catalyst. Importantly, we
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49 found that mounting IrO₂ nanoparticles on Co and N co-doped graphene improved the
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51 catalyst's OER and ORR activity.
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Fig. 6 presents the typical discharge-charge profiles of Li-O₂ batteries with the rGO, Co-N-rGO, or IrO₂/Co-N-rGO cathode for the first 5 cycles in the voltage range of 2.2-4.1 V at the current density of 200 mA g⁻¹. For the first cycle, the IrO₂/Co-N-rGO cathode exhibited the highest Coulombic efficiency of 94.95% as compared with the Co-N-rGO cathode (58.69%) and rGO cathode (15.83%), revealing that the catalytic activity of IrO₂/Co-N-rGO is much higher than Co-N-rGO and rGO, and also comparable to some metal oxide catalysts [27, 28]. Evidently, the performance of the rGO cathode decayed rapidly, as the discharge capacity faded from 9,535 to 280 mAh g⁻¹, and the capacity retention rate was only 2.9% after five cycles. These results could be attribute to the poor ORR/OER catalytic activity of rGO and the undecomposed discharge products block the cathode [11]. By comparison with the rGO, the Co-N-rGO cathode exhibited higher discharge capacity and better capacity retention rate, indicating the enhanced catalytic activity through the doping with Co and N. However, with the IrO₂/Co-N-rGO cathode, the battery exhibited enhanced capacity and capacity retention ability, the reversible capacity is up to 11,731 mAh g⁻¹ after five cycles, and the capacity retention rate is up to 127%, revealing that IrO₂/Co-N-rGO catalyst may undergo an activation process. Both capacity and capacity retention are much higher than the battery without IrO₂ mounting, indicating the significant enhancement of the iridium oxide. Furthermore, our results are actually much better than those of batteries with noble metal-based catalysts as the cathode, reported by other groups previously [20, 29].

Encouraged by the high capacity retention ability of IrO₂/Co-N-rGO, we further

1 examined the cycling performance and energy efficiencies of Li-O₂ cells with
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3 different cathodes at a current density of 200 mA g⁻¹ with a curtailing capacity of 600
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5 mAh g⁻¹. As shown in Fig. 7, the IrO₂/Co-N-rGO cathode exhibited excellent cycling
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7 stability for 200 cycles without obvious degradation. After 200 cycles, the terminal
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9 voltage remained over 2 V and the energy efficiency still above 65%, a superior result
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11 to what other recent studies have reported [30, 31]. Moreover, the charge voltage
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13 plateaus stayed below 4.0 V, which was much lower than those of a Li-O₂ battery with
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15 a carbon/metal composite as the cathode catalyst [32, 33], making this a highly
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17 energy-efficient battery. The cycling stability and energy efficiencies of the
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19 Co-N-rGO cathode was better than that of the rGO cathode, suggesting that doping
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21 with Co and N improved the stability and ORR activity of the catalyst, which is
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23 consistent with the results previous reported [8]. However, this effect may also have
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25 been due to the limited OER activity of Co-N-rGO, which battery performance
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27 degraded rapidly.
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39 IrO₂/Co-N-rGO had high capacity as well as excellent capacity retention ability
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41 and superior cycling stability for the following reasons: (1) the high surface area and
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43 three-dimensional structure of rGO generated high capacity; (2) doping with Co and
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45 N resulted in high ORR performance; and (3) the high dispersion and great promotion
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47 of IrO₂ nanoparticles.
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53 The combined contribution of above three aspects guaranteed the smooth
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55 transportation of oxygen and lithium ions, decreased the charge/discharge
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57 overpotential, and accelerated the decomposition of discharge products, resulting in
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high performance Li-O₂ batteries.

To further understand the excellent ORR/OER activity of IrO₂/Co-N-rGO in catalysing the reversible formation/decomposition of the discharge products, we investigated the changes of electrochemical impedance, morphology, and structure of the IrO₂/Co-N-rGO cathode at different discharge-charge stages. As shown in Fig. 8a, the battery's impedance increased significantly after discharge, indicating that the formation process of insulating discharge products. Interestingly, the battery's impedance almost decreased to the initial value after the battery was recharged, suggesting that the decomposition process of the discharge products. The XRD patterns of the IrO₂/Co-N-rGO cathode (Fig. 8b) indicate the main discharge product is Li₂O₂, which is completely decomposed after the charge process, no any Li₂O₂ peaks could be observed. The EIS and XRD results confirm the efficiently decomposition of the Li₂O₂ product on our catalyst, indicating the superior reversibility of Li-O₂ batteries with IrO₂/Co-N-rGO cathode.

Fig. 8 (c-e) shows the SEM images of the IrO₂/Co-N-rGO electrode and indicates that the discharge products composed of massive nanospheres and toroids Li₂O₂ [34]. These small and well-dispersed Li₂O₂ nanoparticles ensured the space for oxygen diffusion and sufficient electrode-electrolyte interfaces for the electrochemical reaction, made it easier to be decomposed than the large aggregates Li₂O₂. After recharging process, the cathode recovered to the original graphene structure, the Li₂O₂ nanoparticles are completely disappeared, and these results are quite consistent with the EIS and XRD results, further confirming the good reversibility of IrO₂/Co-N-rGO

cathode.

4. Conclusion

In conclusion, by mounting IrO₂ nanoparticles on Co and N co-doped rGO, we successfully prepared a high-performance composite catalyst, IrO₂/Co-N-rGO, for the cathode in Li-O₂ batteries. We found that mounting IrO₂ nanoparticles on co-doped rGO significantly enhanced the catalyst's OER and ORR activity. A battery with this catalyst as the cathode demonstrates very high capacity retention ability and cycling stability: it delivered a high reversible capacity of 11,731 mAh g⁻¹ after five cycles at 200 mA g⁻¹, and maintained 200 stable cycles with limited capacity of 600 mAh g⁻¹. We found that the mounting of IrO₂ nanoparticles, generally known as OER catalyst, not only enhanced the OER activity of the catalyst significantly, but also enhanced the ORR activity obviously through its effects on the co-doped graphene. We suggested that the high capacity, excellent capacity retention ability, and superior cycling stability of the catalyst could be attributable to the high surface area of rGO, the enhanced ORR activity arising from co-doping of Co and N, and the great promotion of IrO₂ nanoparticles. The design and preparation of this composite catalyst may prove helpful in developing efficient catalysts for high-performance Li-O₂ batteries.

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Fig. 1

Fig. 1 The schematic diagram of the structure of the IrO₂/Co-N-rGO cathode catalyst and the possible mechanism for the promotion of IrO₂.

Fig. 2

Fig. 2 XRD patterns (a) and XPS survey spectra (b) of the various catalysts;

high-resolution XPS spectra of IrO₂/Co-N-rGO: (c) N 1s, (d) Ir 4f.

Fig. 3

Fig. 3 SEM (a, b) and TEM (c, d) images of IrO₂/Co-N-rGO; the inset: (d) HRTEM image and the corresponding particle size distribution of IrO₂.

Fig. 4

Fig. 4 STEM images and the corresponding elements EDX mapping images of Co-N-rGO (a-f) and IrO₂/Co-N-rGO (g-l) catalysts.

Fig. 5

Fig. 5 (a) Electrochemical impedance spectra of Li-O₂ batteries with the various cathodes; (b) in situ CV curves of Li-O₂ batteries with the various cathodes between 2.0 and 4.5 V at 0.5 mV s⁻¹ in an oxygen-saturated TEGDME electrolyte.

Table 1 Resistances of Li-O₂ cells with three types of cathodes obtained by fitting the EIS spectra with equivalent circuit.

Sample	rGO	Co-N-rGO	IrO ₂ /Co-N-rGO
Rs (ohm)	17.42	7.349	7.354
Rct (ohm)	121.8	104.4	72.4

Fig. 6

Fig. 6 The discharge-charge profiles of Li-O₂ batteries with (a) rGO, (b) Co-N-rGO, and (c) IrO₂/Co-N-rGO cathode at a current density of 200 mA g⁻¹ in the voltage range 2.2-4.1 V; (d) variations in capacity retention rate for Li-O₂ batteries based on different cathode for the first 5 cycles.

Fig. 7

Fig. 7 (a-c) The discharge-charge cycles of Li-O₂ cells with different cathodes at a current density of 200 mA g⁻¹, with a curtailing capacity of 600 mAh g⁻¹; (d) the corresponding specific energy efficiency after different numbers of cycles.

Fig. 8

Fig. 8 Electrochemical impedance spectroscopy spectra (a) (the inset figure is the corresponding equivalent circuit), XRD patterns (b) of the IrO₂/Co-N-rGO electrode at different discharge-charge stages, discharged to 2.2 V and charged to 4.1 V at 200 mA/g; SEM images of the IrO₂/Co-N-rGO electrode: (c) initial electrode; (d) discharged to 2.2 V at 200 mA g⁻¹; and (e) recharged to 4.1 V at 200 mA g⁻¹.