Micro–meso-macroporous FeCo-N-C derived from hierarchical bimetallic FeCo-ZIFs as cathode catalysts for enhanced Li-O₂ batteries performance

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ABSTRACT

Developing bifunctional catalysts that increase both the OER and ORR kinetics and transport reactants with high efficiency is desirable. Herein, micro–meso-macroporous FeCo-N-C-X (denoted as “M-FeCo-N-C-X”, X represents Fe/Co molar ratio in bimetallic zeolite imidazolate frameworks FeCo-ZIFs) catalysts derived from hierarchical M-FeCo-ZIFs-X was prepared. The micropores in M-FeCo-N-C-X have strong capability in O₂ capture as well as dictate the nucleation and early-stage deposition of Li₂O₂, the mesopores provided a channel for the electrolyte wetting, and the macroporous structure promoted more available active sites when used as cathode for Li-O₂ batteries. More importantly, M-FeCo-N-C-0.2 based cathode showed a high initial capacity (18,750 mAh g⁻¹@0.1 A g⁻¹), good rate capability (7900 mAh g⁻¹@0.5 A g⁻¹), and cycle stability up to 192 cycles. Interestingly, the FeCo-N-C-0.2 without macropores suffered relatively poorer stability with only 75 cycles, although its discharge capacity was still as high as 17,200 mAh g⁻¹@0.1 A g⁻¹. The excellent performance attributed to the synergistic contribution of homogeneous Fe, Co nanoparticles and N co-doping carbon frameworks with special micro-meso-macroporous structure. The results showed that hierarchical FeCo-N-C architectures are promising cathode catalysts for Li-O₂ batteries.

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1. Introduction

As one of the most promising electrochemical energy storage systems, aprotic lithium-oxygen (Li-O₂) battery shows an ultrahigh theoretical energy density, about 5–10 times than that of traditional lithium-ion batteries, and has captured widespread attention [1–3]. However, many scientific challenges, such as poor rate capability, large charge/discharge overpotential and limited cyclic stability, should be overcome prior to the practical applications [4–7]. Intensive research efforts have been devoted to focusing on the optimization of the lithium metal anode, the electrolyte and especially the air catalytic cathode [8–11]. Bruce et al. effectively improved the cycle stability of 95% capacity retention for 100 cycles using a dimethyl sulfide electrolyte and porous gold electrode [9]. Visco et al. have developed an artificial ceramic solid electrolyte interphase (SEI) to protect the anode, in which the cell possessed high cycling ability over 60 times at 0.4 mAcms⁻² in air with 50% relative humidity [12]. Zhou et al. have demonstrated a core-shell structured CNT@RuO₂ composite as cathode catalyst with high round-trip efficiency (ca. 79%), excellent rate and cycling performance [13]. The reaction mechanism of Li-O₂ battery is the reversible transformation of Li₂O₂ formation and decomposition during charge and discharge (2Li⁺ + O₂ + 2e⁻ = Li₂O₂, 2.96 V vs. Li/Li⁺). The air electrode of the battery undergoes an oxygen reduction reaction (ORR) to form Li₂O₂ during discharge, while the electrode undergoes an oxygen emission reaction (OER) to produce O₂ during charge [14]. However, the main product Li₂O₂ and other by-products are mostly insulating and insoluble, which would be difficult to decompose in the charge process and result in large overpotential [15]. Due to the slow kinetics of ORR and OER, it is urgent to design a porous cathode catalyst with more accessible active sites and sufficient channels to improve the capacity and cycle life of the Li-O₂ battery.

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Previous investigations have shown that cathode catalysts mainly include metal oxides [16–18], metal nitride [19,20] and carbon materials (including nanotubes, graphene, etc.) [21–24]. Among them, carbon materials were the most widely developed. The morphologies, size and surface chemistry especially the available active sites of the carbon materials have crucial influence on the performance of Li-O₂ batteries. Doping secondary metals or heteroatoms were significant in promoting the catalytic activity. Specifically, the nitrogen atoms embedded in the carbon not only modified the electron configurations and structural properties of the carbon materials but also stabilized other metal atoms to further enhance the catalytic activity [25,26].

In recent years, metal organic frameworks (MOFs), MOF derivatives and composites were widely used in rechargeable metal-air batteries [23,27,28]. Pristine MOFs used as air electrode showed a higher discharge capacity owning to its high specific surface area, special porous structure and abundant active sites. Our previous study also demonstrated that downsizing Co-MOF-74 with distinct morphologies as cathode materials for Li-O₂ batteries possessed an ultrahigh capacity [29]. However, the poor conductivity and the unstable structure of MOFs restricted the rate capability and cycling performance and also raised the overpotential during charge and discharge. How to further improve the stability of MOFs as Li-O₂ battery cathode catalysts is still a great challenge.

In this regard, much attention has been focused on MOF-derived metal-nitrogen-carbon (M-N-C) catalysts, which feature high catalytic activity and low-cost for ORR & OER in both acidic and alkaline fuel cells [30,31]. The M-N-C materials obtained by heat-treatment of MOFs would further enhance the electrocatalytic performance and maintain the well-defined morphologies with high specific surface area and porous structure to a great extent [32]. Since the air cathode of Li-O₂ battery is similar to fuel cell cathode, M-N-C catalysts are also promising to boost the performance of Li-O₂ batteries. Specifically, M-N-C catalysts derived from MOFs not only optimized of the geometric structures of the materials but guaranteed the durability of the activity [33]. Moreover, catalysts with hierarchical pores extremely stimulated the performance of electrochemical devices, attributing to the special porous structure efficiently transport electron and reactants [34,35]. By drawing comparison between traditional MOFs and hierarchical porous MOFs, the M-N-C derived from the latter ones retained the initial micropores, mesopores and macropores, which largely exposed more active sites benefited from the high surface area as well as eased the way electrons and reactants transfers. Moreover, the micropores in M-N-C have strong capability in O₂ capture as well as dictate the nucleation and early-stage deposition of Li₂O₂, the mesopores provided a channel for the electrolyte wetting, and the macroporous structure promoted more available active sites.

Many studies have shown that cathode catalysts with hierarchical porous structures, especially macropores and mesopores, were extremely important for improving the performance of Li-O₂ batteries [36–39]. The unique hierarchical porous structure of the catalysts with microporous channels will facilitate rapid O₂ diffusion while highly dictate the nucleation and early-stage deposition of discharge products. The mesopores could effectively improve the electrolyte immersion, facilitate Li⁺ diffusion and electron transfer, while the macroporous structure would facilitate kinetic accessibility of the active sites and store more discharge products [40]. However, most of the air-electrodes with macropores were metal oxides [38,41], and the bimetal-nitrogen-carbon (BM-N-C) materials derived from micro–meso-macroporous MOFs used as cathode of Li-O₂ batteries were rare.

In this work, we reported a facile method to prepare FeCo nanoparticles decorated 3D hierarchically N co-doped micro–meso-macroporous carbon composites (M-FeCo-N-C-X) derived from hierarchical FeCo bimetallic MOF (M-FeCo-ZIFs-X) with different iron doping ratios. In this strategy, hierarchical M-FeCo-ZIFs-X precursors were prepared by using polystyrene microspheres as templates. After etching out the templates, M-FeCo-ZIFs-X nanoparticles with uniformly distributed macropores were obtained. Importantly, our research have shown that hierarchically porous M-FeCo-N-C-X especially M-FeCo-N-C-0.2 based cathode showed excellent electrochemical activity better than most of the reported non-noble-metal cathode catalysts. This study offered a promising strategy to design 3D structured micro–micro-macroporous air cathodes for Li-O₂ batteries with high discharge capacity.

### 2. Experimental

#### 2.1. Materials

- **Styrene** \( (C_6H_5CH=CH_2, \text{AR}) \), **sodium dodecyl sulfate** \( (C_{12}H_{25}-OSO_3Na, \text{AR}) \), **potassium persulfate** \( (K_2S_2O_8, \text{AR}) \), **polyvinyl pyrrolidone** \( (\text{PVP}, 30 \text{k}) \), **sodium hydroxide** \( (\text{NaOH}, 96\%) \), anhydrous alcohol \( (\text{C}_2\text{H}_4\text{OH}, \text{AR}) \), **methanol** \( (\text{CH}_3\text{OH}, \text{AR}) \), **FeSO₄·7H₂O (AR) \), **N,N-dimethylformamide (DMF, AR) \), other chemicals purchased from Sigma-Aldrich and were used without further purification.

#### 2.2. Polystyrene sphere template preparation

Polystyrene microspheres (PS) were synthesized according to the method reported previously with minor modification [42]. Typically, 35 mL styrene (ST) was firstly washed with 10 mL 10 wt.% NaOH solution and deionized water to remove the stabilizer. Then, the washed ST was added to 250 mL water with 1.25 g PVP in a triple-neck flask with nitrogen purged for 15 min. Afterward, the mixture was filtered at 60°C with stirring for 30 min and then 20 mL of aqueous solution containing 0.5 g K₂S₂O₈ was injected into the flask to initiate the polymerization reaction of ST. After keeping stirring for 24 h at this temperature, the mixture was cooled down and the obtained milk-like product was then centrifuged 2500rpm for 8 h. The obtained precipitations were then dried at 60°C for 8 h to obtain the PS templates.

#### 2.3. Synthesis of micro–meso–macroporous FeCo-N-C polyhedra

The M-FeCo-N-C-X catalysts were prepared by slightly modified from previously reported methods [43]. In typically synthesis, 0.500 g PS templates, specific feedings of Co(NO₃)₂·6H₂O and FeSO₄·7H₂O were dissolved in 160 methanol to sonicate 60 min. The total amount of substance of metal species kept 3 mmol to obtain the series of target products. The solution was poured into another 160 mL methanol solution containing 3.941 g (48 mmol) 2-methylimidazole under stirring. It is worth noting that methanol should be bubbled with nitrogen before use. Afterward, the solution was continuously bubbled with N₂ and kept at 35°C for 12 h, and the obtained precipitate was centrifuged, washed three times with methanol, generating the M-FeCo-ZIFs-X crystals where \( X = 0, 0.1 \) and 0.2, respectively. The PS templates were removed by etching with fresh DMF for 3 times in 48 h. The product was centrifugated again with DMF and methanol several times and dried at 60°C for 12 h. M-FeCo-N-C-X catalysts via pyrolyzing M-FeCo-ZIFs-X at 800°C for 2 h in nitrogen atmosphere without any post-treatment.

#### 2.4. Material characterization

- Powder X-ray diffraction (PXRD) patterns were performed on an Ultima IV diffractometer (Rigaku Corporation) with Cu Kα radiation.
radiation. The morphologies of the products were obtained using FEI Inspect F50 and Navo Nano SEM450 scanning electron microscope (SEM). The EDX attached to the FESEM instrument was used to confirm the composition of the samples. TEM images were taken on FEI Tecnai G2F-20 equipped with EELS, and XPS was performed on Axis Ultra DLD (Kratos Analytical). N$_2$ adsorption/desorption isotherms were measured at 77 K on a nitrogen adsorption apparatus (Thermo Fisher Scientific Surfert Gas Adsorption Porosimeter) after activating the sample at 100 °C for 10 h under vacuum.

2.5. Li$_2$O$_2$ cell preparation and electrochemical performance measurements

The O$_2$ electrodes were prepared by coating homogeneous slurry composed of a mixture of 45 wt% as-fabricated FeCo-N-C-X catalysts, 45 wt% Ketjen Black (KB), 10 wt% of polyvinylidene fluoride (PVDF) onto a carbon cloth dried in a vacuum oven at 80 °C for 12 h. For comparison, the pure KB electrode was also prepared with 90 wt% KB and 10 wt% PVDF using the same procedure. Li-O$_2$ cells were assembled in a glove box filled with high purity argon, in which the oxygen and moisture concentrations were maintained below 1 ppm, using CR2032-type coin cells with several holes for O$_2$ transportation on the cathode side. Lithium foil was used as anode, a glass fiber filter (Whatman) was used as a separator, and 1 M LiTFSI/0.5 M LiI in DMSO was used as electrolyte. The assembled cells were placed in oxygen and DMSO filled chamber, and were aged for 10 h before the electrochemical measurements.

The Li-O$_2$ batteries were galvanostatically cycled at a current rate of 0.5 A g$^{-1}$ between 2.0 and 4.5 V on a LAND CT2001A battery-testing system. All the capacity and current density values were normalized by the total mass of catalyst and KB.

3. Results and discussion

Scheme 1 illustrates the overall fabrication process of M-FeCo-N-C-X catalysts, which were prepared by simple annealing treatment of bimetallic M-FeCo-ZIFs-X with different iron doping ratios. The polystyrene (PS) microspheres templates with smooth surface and uniform size were synthesized by the method in the literature [42]. As shown in Fig. S1, the microspheres with average diameter of 350 nm were dispersed uniformly without any agglomeration. It was worth noting that the cobalt-iron salt precursor solution could be permeated effectively into the interstitial spaces between the PS assembly through capillary force [44] and 2-methylimidazole solution were subsequently added into the above solution; then the FeCo-ZIFs-X precursors were filled into the PS interstices to form “FeCo-ZIFs-X@PS” monoliths. As a result, the precursors smoothly turned into 3D FeCo-ZIFs-X crystals; finally “FeCo-ZIFs-X@PS” were soaked in fresh DMF for etching PS templates to obtain M-FeCo-ZIFs-X with uniform distribution of macropores.

As shown in Fig. 1(a), the bimetallic M-FeCo-ZIFs-X was successfully synthesized. All samples showed the similar diffraction peak as the simulated ZIF-67 [45] and there were no other diffraction peaks, confirming the formation of phase-pure M-FeCo-ZIFs-X with good crystallinity. M-FeCo-ZIFs-X with different metal molar ratios could be obtained by changing the doping amount of Fe$^{2+}$. Compared with M-Co-ZIF-67, the diffraction peaks of M-FeCo-ZIFs-X shifted slightly as a result of the lattice expansion, which were attributed to the larger ion radius of Fe$^{2+}$ than that of Co$^{2+}$. Strikingly, the structure of the as-obtained product could be classified into a new phase other than ZIF-67 when the molar ratio of Fe/Co reached 0.3. The inability to obtain the bimetallic M-FeCo-ZIF with molar ratios Fe/Co=0.3 may be ascribed to the addition of excess Fe$^{2+}$ in the solution. Excessive Fe ions disrupted the coordination equilibrium of the metal with the organic ligand 2-methylimidazole and further disturbed the controlled growth of the ZIF nanocrystals [46]. In addition, the massive PS templates in the reaction system would change the reaction environment to some extent. Actually, as long as PS templates were added, the terminal product turned out to be the PS templates themselves without generating any FeCo-ZIFs crystals when the molar ratio of Fe/Co reached 0.3. For the sake of explaining the above-mentioned phenomenon, we proposed the following reasons: (1) The pH values of metal salt precursor solution varied from 3.62 to 4.28 after the incorporation of PS templates; (2) By mixing PS templates and the reaction system evenly using ultrasonic, it was unavoidable to bring O$_2$ into the system, which may hindered the formation of FeCo-ZIF-0.3.

The porous texture of M-Co-ZIF-67 and M-FeCo-ZIFs-X has been characterized by N$_2$ adsorption-desorption isotherms at 77 K (Fig. 1b), and similar hysteresis loop of type IV isotherms appeared in all diagrams indicating the coexistence of micropores and mesopores [45,47]. The BET surface areas were 1275 m$^2$ g$^{-1}$, 1157 m$^2$ g$^{-1}$ and 1115 m$^2$ g$^{-1}$ for M-FeCo-ZIFs-X with X to equal to 0, 0.1 and 0.2, respectively. Obviously, the hysteresis loop of M-FeCo-ZIFs-X (X=0.1, 0.2) was more obvious than M-Co-ZIF-67. The result was consistent with SEM spectroscopy analysis (Figs. 2a and S4), that is, the corresponding decrease in BET specific surface area of samples with more macropores. In addition, the specific surface area of M-Co-N-C, M-FeCo-N-C-0.1, M-FeCo-N-C-0.2 derived from M-FeCo-ZIFs-X precursors reached 309 m$^2$ g$^{-1}$, 389 m$^2$ g$^{-1}$ and 401 m$^2$ g$^{-1}$, respectively and typical mesoporous structure.

Scheme 1. Illustration of the overall fabrication process for the M-FeCo-N-C-X catalysts.
of the M-FeCo-N-C-X got rough and wrinkled while remained the original morphology of M-FeCo-ZIFs-X after the high thermal treatment (Figs. 2b and S4). Element mapping of representative M-FeCo-N-C-0.2 indicated the uniform distribution of Fe, Co, N and C, confirming homogeneously substitution of Co²⁺ by Fe²⁺ (Fig. S5). TEM images clearly revealed that the number of macropores was successfully preserved even after the calcined process at 800 °C for 2 h and small Fe, Co nanoparticles were homogeneously distributed within the crystals (Fig. 2c, d). HRTEM further manifested that the Fe and Co nanoparticles were encapsulated by carbon layer with a (002) crystal lattice spacing of 0.341 nm (Fig. 2e). Inside the carbon layer the crystalline Fe, Co nanoparticles had lattice fringe space of 0.132 nm and 0.220 nm corresponding to the (200) and (111) lattice plane respectively, which were consistent with the diffraction ring of the selected area electron diffraction (SAED) pattern (Fig. 2f). X-ray diffraction (XRD) analysis of M-FeCo-N-C-X obtained by post-heat treatment of the M-FeCo-ZIFs-X precursors under inert atmosphere further elucidated that the dominant phase of the composite was metal Co with diffraction peaks centered at 44.21° and 51.52°, which could be assigned to the (111) and (200) facets of Co fcc (JCPDS No. 15-0806). In addition, the diffraction peak centered at 44.67° and 65.02° corresponds to the (110) and (200) plane of Fe bcc (JCPDS No. 06-0696) (Fig. S2).

To explore the chemical properties and the surface states, the high-resolution X-ray photoelectron spectroscopy (XPS) spectra were conducted to the M-FeCo-N-C-0.2 (Fig. 3a). The deconvoluted N 1s spectra showed four types of nitrogen species (Fig. 3b): graphitic-N, pyrrolic-N, pyridinic-N and metal-N [48,49]. As is known, the abundant graphite nitrogen and metal nitrogen could effectively optimize the local electronic structure to improve ORR activity [50]. Moreover, the deconvoluted XPS spectra of Co 2p gave evidence of the Co-N₆ coordination and metallic Co (Fig. 3c). Specially, the deconvolved peaks centered at 780.3 and 795.7 eV with shake up satellites (denoted as “Sat.”) at 786.1 and 802.8 eV were deemed as the cobalt atoms with high valence state, namely Co-N₆ species [51,52]. Fig. 3(d) shows the high-resolution Fe 2p spectrum of the composite. The Fe 2p₁/₂ spectrum was fitted using three components at 709.9 eV (metal iron), 711.7 eV (Fe³⁺ species) and 715.6 eV (satellite of Fe³⁺). The peak at 720.2 eV in the Fe 2p₁/₂ XPS spectrum demonstrated the existence of Fe-N₆ bonding in the prepared sample [53,54]. Both the Metal-N centers and metallic Fe/Co nanoparticles could facilitated the process of Li₂O₂ reaction [55,56]. It is well known that the adsorption energies of O₂ on the M-N₆ coordination sites are efficient to initiate the ORR [57]. Besides, the active Fe, Co species can work as the OER catalytic sites which benefit from the enhanced charge transfer from Li₂O₂ to Metal (Fe, Co) to further decompose the Li₂O₂ [58]. Overall, XPS analysis demonstrated the homogeneous metal species distribution, N-doping and strong metal-N coordination were expected to contribute significantly to improvement of ORR and OER activity.
Fig. 3. XPS survey spectra of (a) M-FeCo-N-C-0.2, high-resolution of (b) N 1s, (c) Co 2p and (d) Fe 2p.

Fig. 4. (a) First charge–discharge curves and (b) first discharge curves of Li–O$_2$ cells with pure KB, M-Co-N-C/KB, M-FeCo-N-C-0.1/KB and M-FeCo-N-C-0.2/KB electrodes at a current density of 0.1 A g$^{-1}$. (c) Discharge specific capacity of Li–O$_2$ cells with the four kinds of O$_2$ electrodes at different current densities. (d) Cyclic performance of Li–O$_2$ cells with M-FeCo-N-C-0.2/KB, M-FeCo-N-C-0.1/KB and M-Co-N-C/KB.
The performances of Li-O$_2$ batteries with M-FeCo-N-C-X catalysts were investigated by using 2032-type coin cells with 1 M LiTFSI/0.5 M LiI in DMSO as an electrolyte. For comparison, the O$_2$-electrodes with pure KB were also tested under identical conditions. As shown in Fig. 4(a), the full discharge/charge profiles of the O$_2$-electrode with the M-FeCo-N-C-X ($X = 0.2$, 0.1)/KB and M-Co-N-C/KB catalysts for the first cycle were measured at a current density of 0.1 A g$^{-1}$ between 2.0 and 4.5 V (versus Li/Li$^+$) at room temperature. The electrode with M-FeCo-N-C-X/KB presented much higher specific capacity and much lower median overpotential than the other O$_2$-electrode. Compared with pure KB (10,790 mAh g$^{-1}$), the cathode catalyzed by M-FeCo-N-C-0.2 had the lowest overpotential and promoted discharge specific capacity (18,750 mAh g$^{-1}$), which indicated that the modification of M-FeCo-N-C enhances ORR and OER activity. It was remarkable that differences of the charge voltage profile among the different
electrodes might possibly result from the different forms of Li$_2$O$_2$ on electrodes as well as certain complicated by-products [38,59]. The discharge capacity was close to the charge capacity, it was a signal that the Li$_2$O$_2$ product after discharge could be reversibly converted to Li and O$_2$ [60]. Note that stable full discharge/charge cyclability is typically hard to realize due to the accumulation of the discharge product and instability of the electrolyte [32,61]. Fig. 4(b) shows the discharge curves of Li-O$_2$ cells utilizing the M-FeCo-N-C-X cathodes at a current densities of 0.1 Ag$^{−1}$. It was obvious that the battery cathode catalyzed by M-FeCo-N-C-0.2 (18,750 mAh g$^{−1}$) exhibited a much higher initial capacity than M-FeCo-N-C-0.1 (16,800 mAh g$^{−1}$), and M-Co-N-C (14,820 mAh g$^{−1}$). With the increasing content of Fe, the discharge capacity gradually elevated; the result was consistent with the full discharge/charge curve, indicating that the incorporation of iron upgraded the discharge capacity effectively. The rate performance of the Li-O$_2$ cells was further examined. The differences of the initial capacity for M-Co-N-C, M-FeCo-N-C-0.1 and M-FeCo-N-C-0.2 based cathodes became larger under a higher current density. Under a current density of 0.5 Ag$^{−1}$, the battery catalyzed by M-FeCo-N-C-0.2 still delivered a higher initial capacity of 7900 mAh g$^{−1}$, much higher than that of M-FeCo-N-C-0.1 and M-Co-N-C (Fig. 4c). When it comes to cycle stability and durability, M-FeCo-N-C-0.2 based catalyst could stay up to 192 cycles. M-FeCo-N-C-0.1 and M-Co-N-C based O$_2$-electrode also could stick to 94 cycles and 56 cycles, respectively (Fig. 4d).

As a comparison, FeCo-N-C-0.2 with uniform rhombic dodecahedron morphology was synthesized by the same method, except that PS templates were not added (Fig. 5a and f). When FeCo-N-C-0.2 without macropores was used as the cathode catalyst of Li-O$_2$ battery, the discharge specific capacity was still as high as 17,220 mAh g$^{−1}$, but its stability was comparatively poor (only 75 cycles) (Fig. 5). The results showed that FeCo-N-C-X catalyst could effectively improve the discharge capacity of the battery. In particular, the special macropores were beneficial to store the discharge product and accelerate the transmission of electrolyte and oxygen, thus improving the cycle stability of the battery. The results presented herein demonstrated that macropores were necessary for Li-O$_2$ battery cycle stability.

For the M-FeCo-N-C-0.2 based battery, its cycling stability and terminal voltage versus cycle number were further evaluated with a fixed capacity of 800 mAh g$^{−1}$ at a current density of 0.5 Ag$^{−1}$, as shown in Fig. 6(a). The profiles of the first 50 cycles illustrated that the cell operated efficiently with slightly lower voltage, indicating that Li$_2$O$_2$ could be reversibly decomposed and generated in macropores. As the cycle progresses, the potential gradually increases, but it still stably cycled to 194 cycles. In addition, the overpotentials of the OER and OER in the M-FeCo-N-C-0.2 based battery were slightly lower than those in the M-Co-N-C@Li-O$_2$ at 0.5 Ag$^{−1}$, as shown in Fig. 6(b). In contrast, the cycle performance and overpotential of macroporous M-FeCo-N-C-0.1 and M-Co-N-C were far behind with M-FeCo-N-C-0.2, especially M-Co-N-C without Fe element doping only stayed up to 56 cycles and the overpotential suddenly increased a lot. The catalysts were easily passivated during long-term use when directly exposed to oxygen in the electrolyte, due to the continuous accumulation of discharge and charge products during cycling.

Fig. 7 shows the SEM images of M-FeCo-N-C-0.2 based cathodes under different discharge states. Before discharge, it could be clearly observed that the polyhedron catalysts were uniformly mixed with KB on the cathode (Fig. 7a). When the catalysts underwent full discharge, the catalysts were covered by a layer of irregular solid discharge products. Some irregular products formed on the cathode catalyzed by M-FeCo-N-C-0.2, as shown in Fig. 7(c, d). The results indicated that M-FeCo-N-C-X catalysts had an important effect on the discharged products and the modification of M-Co-N-C by Fe promoted the formation of the discharged product, which benefited the OER. Aside from the large surface area, co-doping of Fe, Co and N, the enhanced activity was also related to the mixed macro–meso-microporous structure, which facilitated the accessibility of O$_2$ and transport of by-products.

4. Conclusions

In summary, hierarchical micro–meso-macroporous Fe, Co co-doping carbon-nitrogen architectures were prepared by a rational and facile strategy. When employed as cathode catalysts in rechargeable Li-O$_2$ batteries, the M-FeCo-N-C-0.2 suppresses the OER and especially OER overpotentials in DMSO-based electrolytes. Moreover, the M-FeCo-N-C-0.2 exhibited a high discharge capacity of 18,750 mAh g$^{−1}$, which was higher than the most previously reported non-noble catalysts and possessed long cycling stability of 192 cycles. Despite the fact that the FeCo-N-C-0.2 without macropores achieved the similar discharge capacity, the cycling stability was comparatively poor (75 cycles). The results further demonstrated that the incorporation of Fe effectively promoted the discharging capacity of the battery, on the other hand, the macropores not only promoted kinetic accessibility to the available active sites but stored more discharge products as well as by-products. That is, the improved Li-O$_2$ cells performance which was considered to stem from the synergistic effect of high catalytic activity and micro–meso-macroporosity of the M-FeCo-N-C-X catalysts. This significant progress provides a new outlook for application of M-FeCo-N-C derived from MOFs for advanced rechargeable Li-O$_2$ batteries.

**Declarations of interest**

None.

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**Supplementary materials**

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