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SHORT COMMUNICATION

Study on leaf-shaped cobalt-based metal-organic frameworks synthesized by solvothermal method as high discharge current density air cathode catalyst for lithium-oxygen batteries

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Abstract
A type of leaf-shaped cobalt-based metal-organic framework material is synthesized by solvothermal method with 1.3:1 cobalt and terephthalic acid ratio and uses as the air electrode catalyst for lithium-oxygen batteries working at high discharge current density. Physical characterization displays that the interaction between cobalt and terephthalic acid can produce a crystal material and the different proportions have a certain influence on their structure and crystallinity. In addition, micromorphology with cobalt and terephthalic acid 1.3:1 shows a leaf-like structure, and synaptic structure on the leaf surface may be beneficial to improve the catalytic activity. Electrochemical tests present that air electrode using this leaf-like structure catalyst materials has good reversibility and the specific discharge capacities can achieve to 3573.90 mAh g^{-1} at 0.5 mA cm^{-2} current densities. However, compared with existing catalysts, these leaf-shaped catalyst materials have no obvious advantage in improving the cycle life.

Keywords Lithium-oxygen batteries · Co-MOF materials · Leaf shape · High discharge current density · Solvothermal method

Introduction

Because of the environmental pollution, the large consumption of fossil fuel, and the rapid development of new energy industry, the rechargeable batteries such as lithium-ion batteries, lead-acid batteries, and supercapacitors [1–7] have been an important development content. Among these, lithium-oxygen batteries owing to its low cost, high theoretical energy densities, and being environmentally friendly have attracted remarkable consideration over the past decade [8–12]. High energy densities which rival that of petrol make the lithium-oxygen battery as one of the ideal power systems for electric vehicles. However, at present, the practical application of lithium-oxygen battery has been limited because of low coulombic efficiency, poor rate capability, and short cycle life. Air electrode is an important aspect of lithium-oxygen battery and a place for electrocatalytic reaction of oxygen reduction and oxygen oxidation. It is widely considered that a highly active catalyst with excellent material composition and structure will come through a rapid electrocatalytic reaction process [13–15].

Precious metals and transition metal compounds are considered as an ideal electrocatalytic material and widely applied to various areas such as environment and energy [16–18]. However, transition metal compounds owing to the low cost and various components and structures have become the main catalytic material for the air electrode of lithium oxygen battery. By changing the catalyst structure or selecting the appropriate composite matrix material, the efficient and rapid oxygen catalytic reaction can be realized, and then an exceptional performance air electrode active material will be successfully obtained. Wang et al. [19] obtained a bi-functional electrocatalyst utilizing Co-doped manganese dioxide/carbon nanotube (CNT) in order to improve the electrochemical performances of zinc-air battery. They found that the rechargeable zinc-air batteries can stably operate for 22 h at a high-current density and show a maximum voltage gap of 1.5 V between charge and discharge voltages. Therefore, the structure and properties of catalysts have become one of the important directions in the research of lithium-oxygen batteries [20–23].

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Cobalt-based metal compounds such as $LiCoO_2$ [24] and Co_3O_4 [25] can be used as excellent active materials for energy storage devices due to their excellent electrical conductivity and electrochemical reversibility. At the same time, they can also be used as the oxygen oxidation and reduction catalyst in the air electrodes of lithium-oxygen battery. Shen et al. [26] presented a novel cobalt-metal-based free-standing cathode for lithium-oxygen battery. Through physical characterization and electrochemical test, it shows that the cobalt metal catalyst can improve the conductivity of the electrode and the metal-based electrodes can deliver high discharge capacity with relatively low overpotential and long cycle life. Hyun and Shanmugam [27] presented Co-CoO nanoparticles embedded in the nitrogen-doped carbon nanorods as a bifunctional air electrode for lithium-oxygen battery. Electrochemical test results illustrate that the air electrode has a high discharge specific of 10,555 mAh g^{-1} at 100 mA g^{-1} and over 86 cycles without a capacity loss.

Metal-organic frameworks (MOFs) are metallic nodes interlinked by electron-donating organic linkers with outstanding porous, crystal structure, and special fuctionalization and utilized in catalysis [28, 29] and energy storage [30–34]. They also have high catalytic activity and can be commonly used in lithium-oxygen battery [35]. In this paper, cobalt-based metal-organic frameworks (Co-MOFs) are synthesized by a facile solvothermal method, and physical and electrochemical tests show that cobalt complexes can form leaf shape and the air electrodes with this catalyst have appreciable specific capacities at high current density.

Experimental

Synthesis of leaf-shaped cobalt-based metal-organic frameworks

Firstly, cobalt acetate and terephthalic acid were weighed according to a certain molar ratio and separately dissolved in 15 ml *N*,*N*-dimethylformamide in order to obtain solution *A* and *B* after ultrasounding for 30 min. And then, solution *A* was slowly dropped to solution *B* and ultrasound again for 30 min in order to receive mixed solution *C*. After that, the mixed solution *C* was transferred to 50 ml autoclave heating at 150 °C for 18 h. Finally, leaf-shaped Co-MOFs can be achieved after centrifugation, washing, and drying. In this paper, the mole ratios of cobalt and terephthalic acid were respectively 1:1, 1.1:1, 1.3:1, and 2:1.

Preparation of air electrode and experimental lithium-oxygen batteries assembly

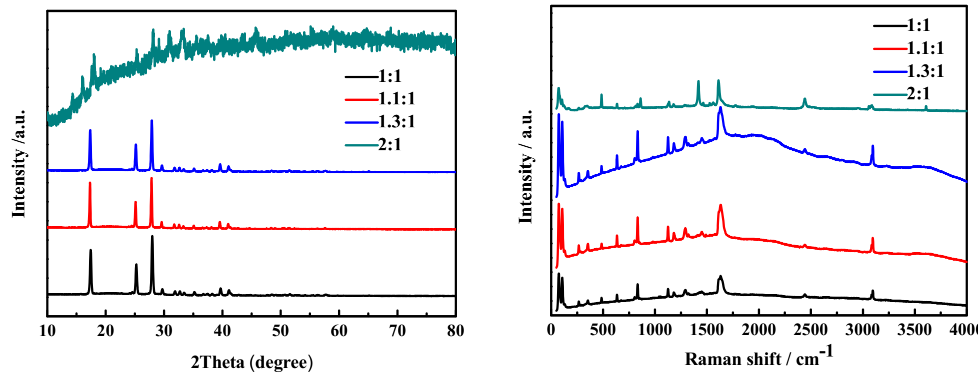
In this experiment, air electrode is similar to traditional. Firstly, the carbon paper was soaked into 5% polytetrafluoroethylene (PTFE) emulsion for 30 min and heated at 350 °C for 5 min. After that, the carbon paper was hydrophobic and can be acted as supporting layer for air electrode. And then, conductive carbon black (Super-P) and 5% PTFE emulsion according to mass ratio 8:2 was fully dispersed in deionized water and evenly sprayed on the abovementioned carbon paper surface in order to compose a stable leveling layer. Then, Super P, catalyst, and 5% Nafion were weighed depending on the mass ratio of 7.5:2:0.5 and evenly dispersed in a mixture of isopropanol and water with a mass ratio of 1:1 by ultrasonic for 2 h. Spray the obtaining slurry on the carbon paper with supporting layer and leveling layer at 60 °C, and at last, air electrode can be achieved after drying at 60 °C for over 24 h. In this experiment, the catalyst consisted of Co-MOF materials and Pt/C. The diameter and total load of air electrode were respectively 10 mm and 1 mg.

In this experiment, the battery assembly process was also the same as our previous research [36]. The air electrode with Co-MOF catalyst as cathode, 0.45-mm-thick lithium foil as anode, super absorbent glass fiber paper (Whatman GF/A) as separator, 1 M lithium bis(trifluoromethanesulphonyl)imide (LiTFSI) in tetraethylene glycol dimethyl ether as electrolyte, and Ni foam and stainless steel as filler were assembled into 2025-button experimental batteries in the glove box filled with high pure argon gas.

Physical characterization and electrochemical performance test

The physical properties of Co-based MOF catalyst materials were confirmed by field emission scanning electron microscope (FE-SEM), X-ray diffraction (XRD), and Raman spectrum tests. The FE-SEM used was S4800 type equipment produced by Hitachi Company. XRD test was conducted with a D Max-RD12 Kw diffractometer with Cu Kα radiation using Rigaku Ultima IV. The scan data were collected in the 2θ rang 10–80° at a scan rate of 2°min^{-1}. The Raman spectrum information was obtained by Labram HR Evolution type Raman Spectrometer produced by Horiba Company. The wavelength of the light source was 532 nm, and the wave number range was from 50 to 4000 cm^{-1}.

The electrochemical performances of experimental lithium-oxygen batteries with Co-MOFs as catalyst for air electrode were tested by contact current charge and discharge, cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS) tests. The contact current charge and discharge test was performed by Neware (CT-4008-5V10mA-164) charging and discharging test system at different current densities from 4.5 to 2.0 V voltage range. CV and EIS tests were carried out by CHI604E electrochemical workstation with air electrode as work electrode and lithium foil as auxiliary and reference electrodes. The CV test voltage range was from 2.0 to 4.5 V at a scan rate of 0.1, 0.2, and 0.5 mV s^{-1}. And the frequency range of EIS was from 100 KHz to 10 mHz with the 5 mV amplitude.



(a) XRD (b) Raman

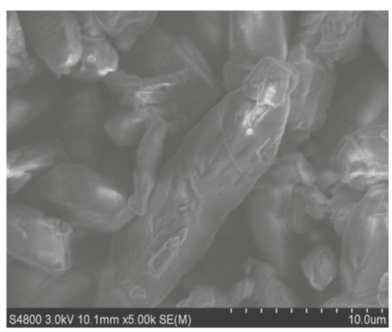
Fig. 1 XRD patterns and Raman spectrum of Co-MOFs with different proportions of organic ligands (**a** XRD, **b** Raman)

Results and discussion

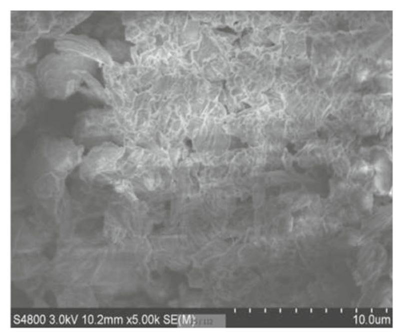
In order to explore the structure of Co-MOFs with different proportions of organic ligands, XRD and Raman measurements were carried out, and the corresponding experimental results are shown in Fig. 1. From XRD patterns (Fig. 1a), it can be found that a type of crystal material can be successfully obtained by solvothermal method, and there are three obvious diffraction peaks (17.37°, 25.18°, and 27.78°) with 1:1, 1.1:1, and 1.3:1 cobalt and terephthalic acid ratio by means of interaction between cobalt and carbon oxides according to PDF#47-0797. This can be proved that Co-MOF materials can be synthesized in this experiment. However, when the proportion of cobalt in the Co-MOF materials is substantially increased (2:1), it shows that the crystallinity of the Co-MOF material decreases obviously and a large number of cobalt carbonate ($CoCO_3$ PDF#11-0692) diffraction peaks have appeared clearly.

Raman spectrum results show that there are a good many of scatting peaks at 71.57, 108.15, 270.11, 366.24, 477.01, 625.39, 838.55, 1134.27, 1186.52, 1297.28, 1444.61, 1629.57, 2448.79, and 3090.38 cm^{-1}. The Raman shifts at 71.57, 108.15, 270.11, 366.24, and 477.01 cm^{-1} signify cobalt metal properties in the Co-MOFs. And other Raman scatting peaks mean benzene ring structure corresponding to terephthalic acid organic ligands. This displays that organic ligand compounds can be successfully formed between cobalt and terephthalic acid by a facile solvothermal method. By comparing different proportion organic ligands, it also can be shown that the content of cobalt determines the crystallinity

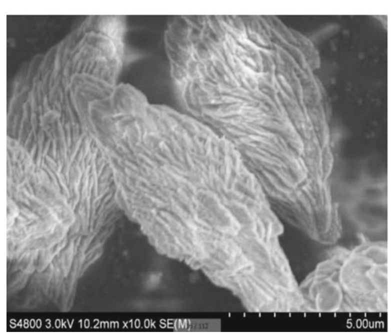
Fig. 2 SEM images of Co-MOFs with different proportions of organic ligands (**a** 1:1, **b** 1.1:1, **c** 1.3:1, **d** 2:1)



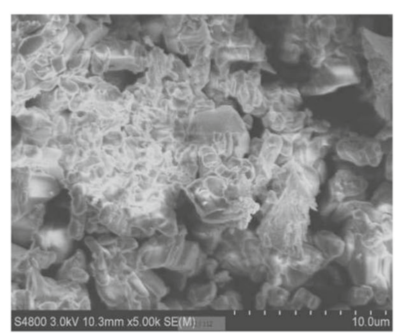
(a) 1:1



(b)1.1:1



(c) 1.3:1



(d) 2:1

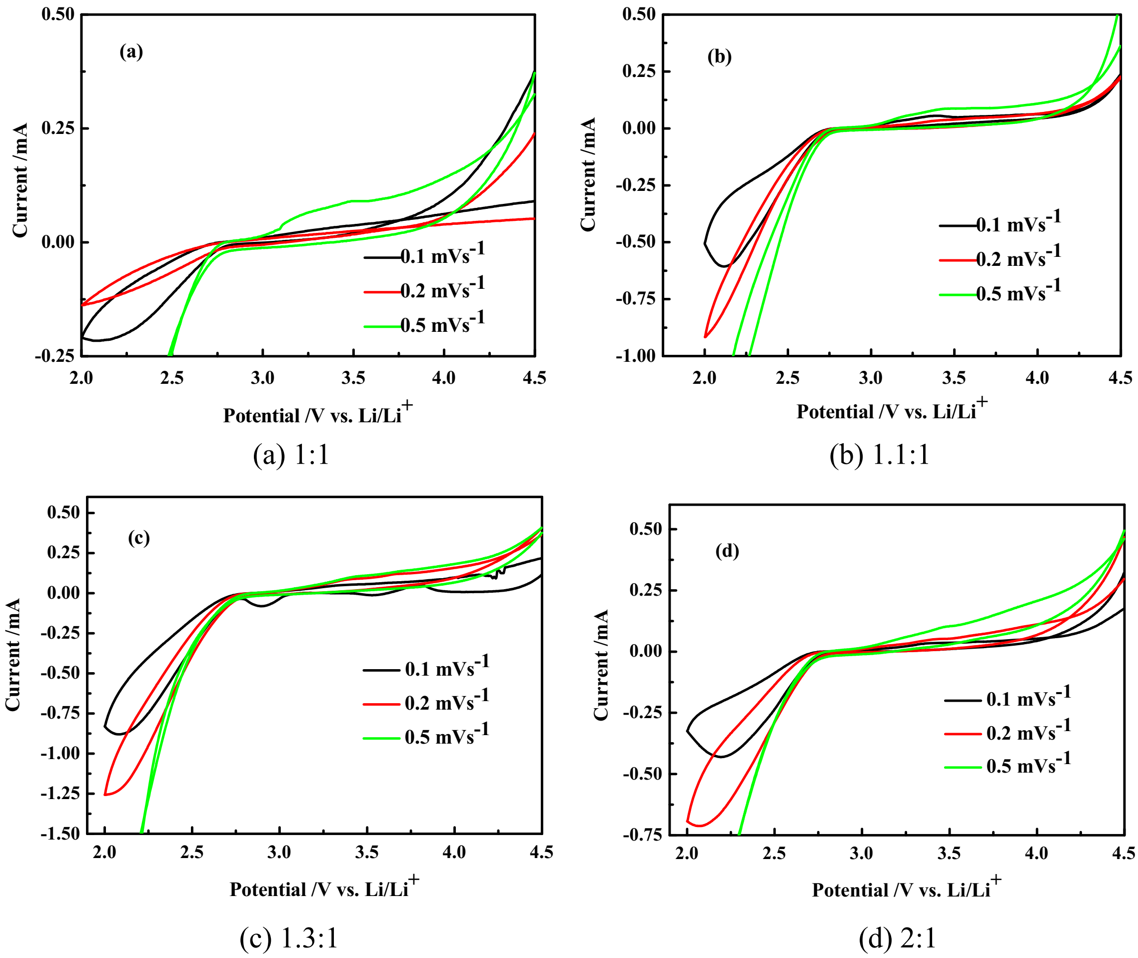


Fig. 3 Cyclic voltammetry curves of air electrode using Co-MOFs as catalyst with different proportions of cobalt and organic ligands (**a** 1:1, **b** 1.1:1, **c** 1.3:1, **d** 2:1)

of the Co-MOFs, and when the ratio of cobalt and terephthalic acid is 2:1, the Co-MOFs have relatively low crystallinity.

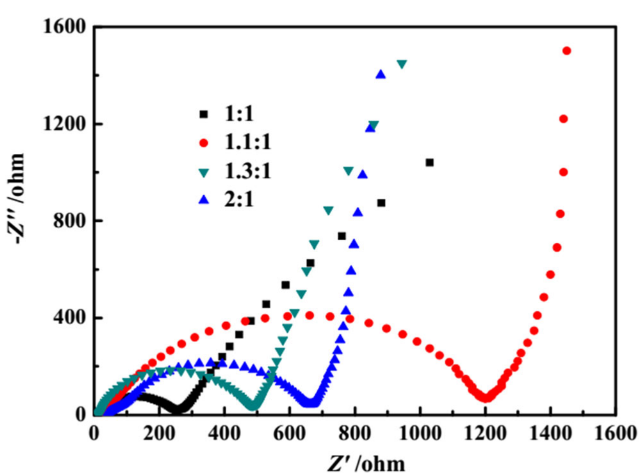


Fig. 4 Nyquist plots of the air electrodes at the open circuit potential using Co-MOF materials as catalyst with different proportions of cobalt and organic ligands

Figure 2 shows SEM images of Co-MOFs with different proportions of organic ligands. It can be observed that the micromorphology of Co-MOFs changed obviously with the different proportions of Co and terephthalic acid organic ligands. When the ratio of cobalt and terephthalic acid is 1:1, the Co-MOF material shows a rod-like structure. However, the Co-MOFs with 1.1:1 and 2:1 cobalt and terephthalic acid ratio have a shape similar to block or sheet. When the ratio of cobalt and terephthalic acid is 1.3:1, the micromorphology of Co-MOFs shows a leaf-like structure and the synaptic structure on the leaf surface will help to improve the catalytic activity.

In order to explore the reversibility of air electrode for lithium-oxygen batteries, cyclic voltammetry test can be presented in this experiment and the cyclic voltammetry cycles are shown in Fig. 3. From the figure, it can be found that there is a pair of oxidation and reduction peaks at 3.5 and 2.3 V (vs. Li/Li$^+$). By exploring the cyclic voltammetry curves at different scanning speeds, it can be found that except for the Co-MOF materials whose ratio of cobalt to organic ligand is 1:1, the curve shapes and peak potentials all have little change, especially the ratio of cobalt to organic ligand is 1.3:1. This

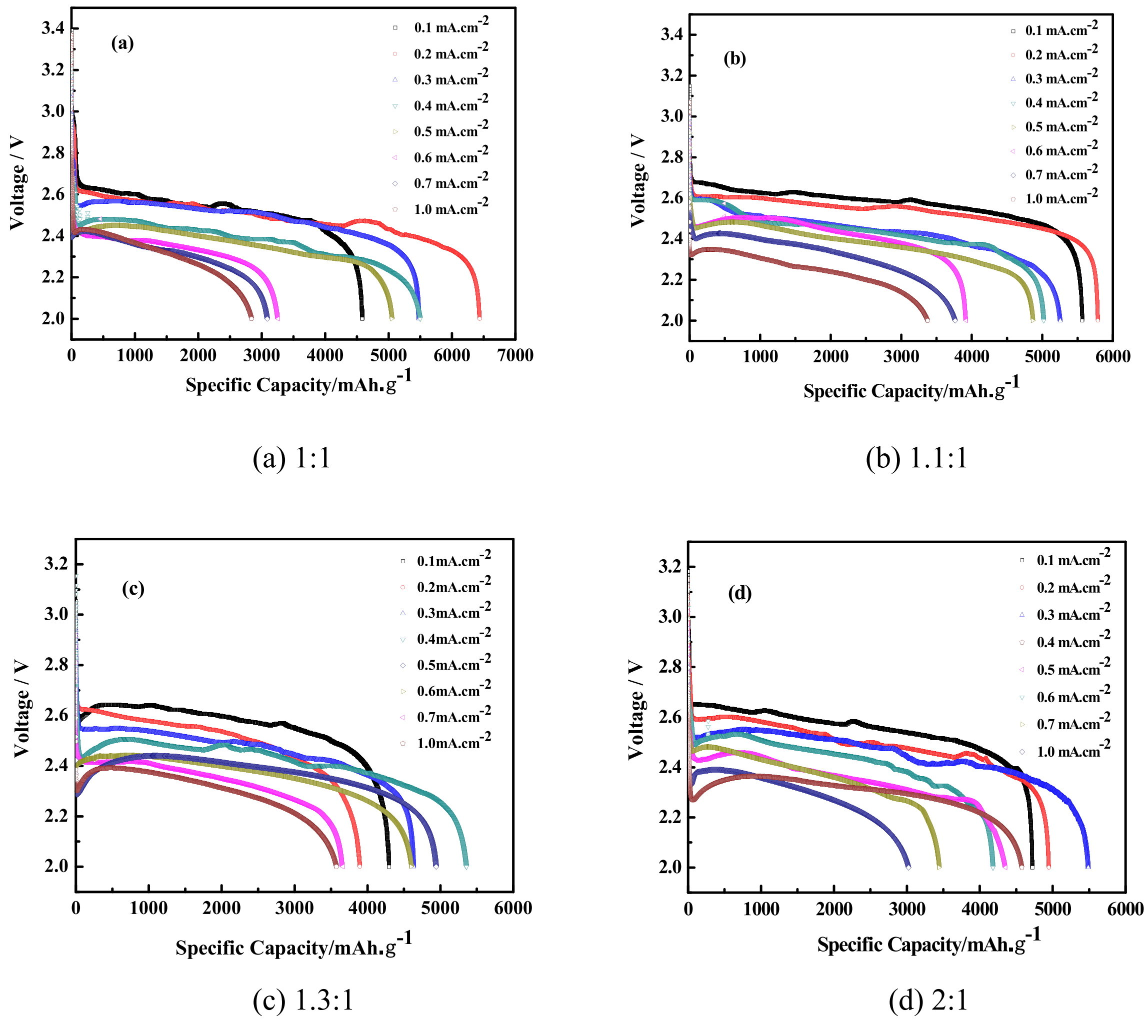
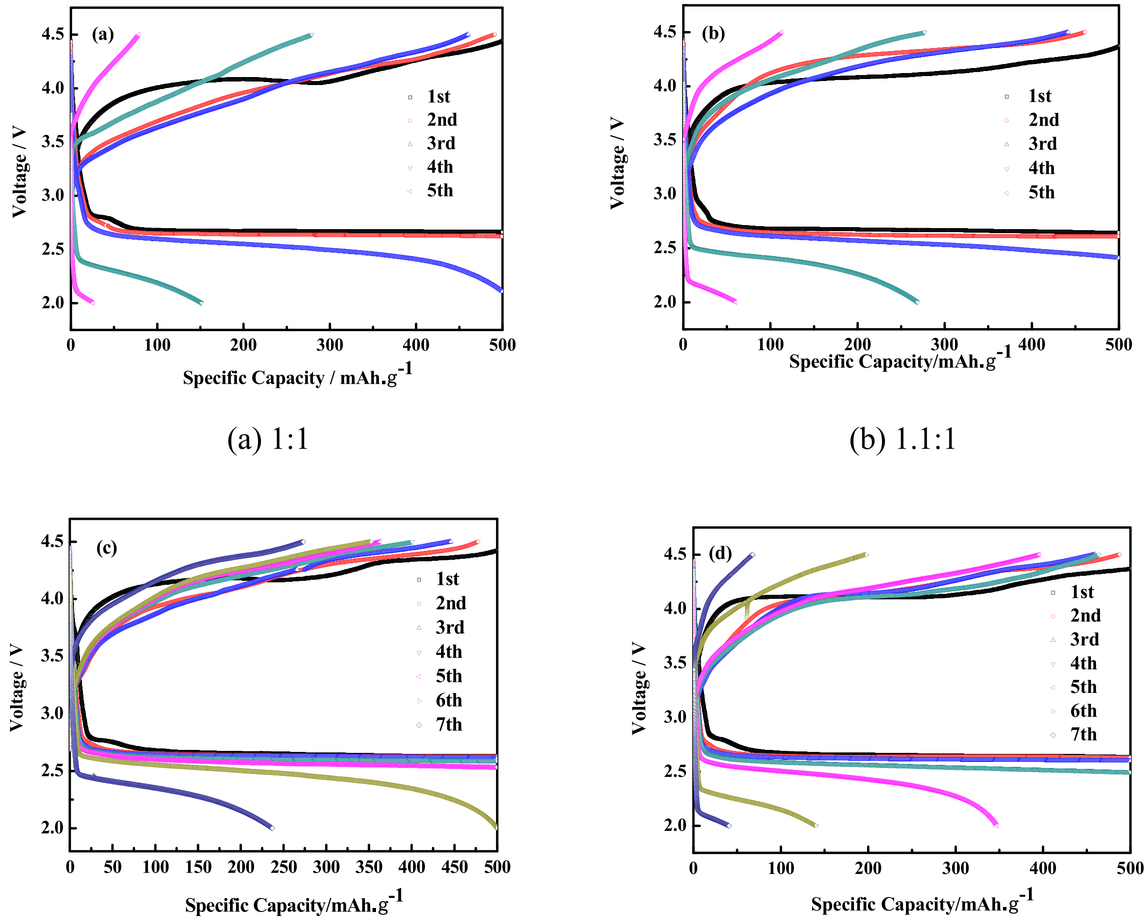


Fig. 5 Initial discharge curves of the air electrodes using Co-MOFs as catalyst with varied proportions of cobalt and organic ligands at different current densities (**a** 1:1, **b** 1.1:1, **c** 1.3:1, **d** 2:1)

means that the air electrodes with Co-MOF materials as catalyst have high reversibility and low overpotential. Therefore, this can be inferred that Co-MOF materials possess high catalytic activity and conductivity and very suitable for the air electrodes of lithium-oxygen battery working at high discharge current densities.

Figure 4 shows Nyquist plots of the air electrodes at the open circuit potential using Co-MOF materials as catalyst with different proportions of cobalt and organic ligands. It displays that air electrodes of lithium-oxygen batteries using Co-MOFs as catalyst show a very complex process of charge and mass transfer due to the influence of cobalt content on the structure of Co-MOF catalyst. By comparison with the impedance arc in the high-frequency region and the straight line in the low-frequency region, we can know that the Co-MOFs with 1:1 cobalt and terephthalic acid ratio have the least charge transfer resistance but the slowest mass transfer speed. By contrast, when the ratio of cobalt and terephthalic acid is 1.1:1, the air electrode has the highest charge transfer resistance but the quickest mass transfer speed. However, air electrodes with leaf-shaped Co-MOF materials as catalysts have high conductivity and lithium-ion transfer rate. Therefore, it is very suitable for the air electrode of lithium-oxygen batteries.

Initial discharge curves of the air electrodes using Co-MOF materials as catalyst with varied proportions of cobalt and organic ligands at different current densities are shown in the Fig. 5. It can be found that air electrodes using Co-MOF materials as catalyst with varied proportions of organic ligands at 1.0 mA cm^{-1} current density all have more than 3000 mAh g^{-1} specific capacity. The specific discharge capacities of the air electrodes using leaf-shaped Co-MOF materials as catalyst can be respectively achieved to 4296.75, 3897.59, 4632.76, 5356.32, 4941.55, 4596.33, 3661.69, 3573.90 mAh g^{-1} at current density from 0.1 to 1.0 mA cm^{-2}, and they have the flatter discharge platforms and lower polarization resistance. This suggests that the leaf-shaped Co-MOF material has more ideal catalytic activity and excellent electrochemical performances for air electrodes of lithium-oxygen batteries at high discharge current densities.



(a) 1:1 (b) 1.1:1

(c) 1.3:1 (d) 2:1

Fig. 6 Cycle life curves of the air electrodes using Co-MOFs as catalyst with varied proportions of cobalt and organic ligands limiting discharge-specific capacity at 500 mAh g^{-1} under 0.5 mA cm^2 current densities (**a** 1:1, **b** 1.1:1, **c** 1.3:1, **d** 2:1)

Cycle life is also an important index of lithium-oxygen battery, and cycle life curves of the air electrodes using Co-MOFs as catalyst with varied proportions of cobalt and organic ligands limiting discharge-specific capacity at 500 mAh g^{-1} under 0.5 mA cm^2 current densities are presented in the Fig. 6. It can be found that the specific discharge capacities of air electrodes using leaf-shaped Co-MOF materials as catalyst can be maintained about 50% initial discharge capacity after 7 times charge and discharge cycles, and this means that the air electrode at this condition has relatively stable charge-discharge stability. However, combined with their initial specific discharge capacities (Fig. 5) and other existing catalysts for lithium-oxygen batteries [31–33], we can conclude that Co-MOF materials can improve the specific capacity of air electrode for lithium-oxygen batteries at high discharge current density more effectively but do not act as an ideal catalyst material for improving cycle life due to only 7 times stable charge and discharge cycles.

Conclusions

In this paper, a type of leaf-shaped cobalt-based metal-organic framework material is synthesized by a facile solvothermal method with 1.3:1 cobalt and terephthalic acid ratio and used as the air electrode catalyst for lithium-oxygen batteries working at high discharge current density. Through XRD, Raman, and SEM test, it can be discovered that cobalt and terephthalic acid in the Co-MOF materials can produce obvious interactions, and the different proportion of cobalt and organic ligands will have a certain influence on their structure and crystallinity. SEM observation displays that the micromorphology of Co-MOFs has been changed obviously at different ratios of cobalt and terephthalic acid organic ligands, and when the ratio of cobalt and terephthalic acid is 1.3:1, the micromorphology shows a leaf-like structure and the synaptic structure on the leaf surface can be beneficial to improve the catalytic activity. Cyclic voltammetry and electrochemical impedance spectroscopy tests illustrate that the air electrode using these leaf-shaped Co-MOF materials as catalyst has good reversibility, high conductivity, and lithium-ion transfer rate. Constant current charge and discharge tests illustrate that the air electrodes using leaf-shaped Co-MOF materials still have high specific discharge capacity even at high discharge current density. However, through cycle life test, limiting discharge-specific capacities at 500 mAh g^{-1} under 0.5 mA cm^2 current densities, it can be found that although the air electrodes using leaf-shaped Co-MOF materials as catalyst can be maintained about 50% initial discharge capacity after 7 times charge and discharge cycles, compared with their initial specific discharge capacities and other existing catalysts for lithium-oxygen batteries, Co-MOF materials have no obvious advantage in improving cycle life.

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References

1. Lang X, Zhao Y, Cai K, Li L, Chen D, Zhang Q (2019) A facile synthesis of stable TiO_2/TiC composite material as sulfur immobilizers for cathodes of lithium-sulfur batteries with excellent electrochemical performances. Energy Technol 7(12):201900543
2. Hu Y, Yang J, Hu J, Wang J, Liang S, Hou H, Wu X, Liu B, Yu W, He X, Kumar RV (2018) Synthesis of nanostructured PbO@C composite derived from spent lead-acid battery for next-generation lead-carbon battery. Adv Funct Mater 28(9):1705294
3. Yu Y, Guo Y (2019) Cerium oxide-modified lithium chromium titanate as high-performance anode material for lithium-ion battery. Ionics 25:367–371
4. Li H, Liu A, Ren X, Yang Y, Gao L, Fan M, Ma T (2019) A black phosphorus/Ti_3C_2 MXene nanocomposite for sodium-ion batteries: a combined experimental and theoretical study. Nanoscale 42: 19862–19869
5. Cai K, Li YY, Lang X, Li L, Zhang Q (2019) Synergistic effect of sulfur on electrochemical performances of carbon-coated vanadium pentoxide cathode materials with polyvinyl alcohol as carbon source for lithium-ion battery. Int J Energy Res 43:7664–7671
6. Yang J, Wang B, Jin F, Ning Y, Luo H, Zhang J, Wang F, Wang D, Zhou Y (2020) MIL-47(V) derived hierarchical lasagna-structured V_2O_3@C hollow microcuboid as an efficient sulfur host for high-performance lithium-sulfur batteries. Nanoscale. https://doi.org/10.1039/C9NR10491G
7. Yusof YM, Shukur MF, Hamsan MH, Jumbri K, Kadir MFZ (2019) Plasticized solid polymer electrolyte based on natural polymer blend incorporated with lithium perchlorate for electrical double-layer capacitor fabrication. Ionics 25:5473–5484
8. Mu S, Zhu D, Zhang R, Zhang K, Ding Z, Chen Y (2018) A lithium ion/oxygen hybrid battery with high energy and high power. Chem Commun 54:8112–8115
9. Wang X, Wang Q, Hou X, Liu Y, Zheng P, Huo J, Yin L, Guo S (2018) Facile fabrication of two-dimensional reduced graphene oxide/CoAl-layered double hydroxides nanocomposites for lithium-oxygen battery with improved electrochemical performance. J Alloys Compd 744:196–203
10. Wang KX, Zhu QC, Chen JS (2018) Strategies toward high-performance cathode materials for lithium-oxygen batteries. Small 14(27):1800078
11. He K, Bi X, Yuan Y, Foroozan T, Song B, Amine K, Lu J, Shahbazian-Yassar R (2018) Operando liquid cell electron microscopy of discharge and charge kinetics in lithium-oxygen batteries. Nano Energy 49:338–345
12. Zhang K, Mu S, Liu W, Zhu D, Ding Z, Chen Y (2019) A flexible NASICON-type composite electrolyte for lithium-oxygen/air battery. Ionics 25:25–33
13. Lang X, Zhang Y, Cai K, Li L, Wang Q, Zhang Q (2019) High performance CoO nanospheres catalyst synthesized by DC arc discharge plasma method as air electrode for lithium-oxygen battery. Ionics 25(1):35–40
14. Wang B, Ruan T, Chen Y, Jin F, Peng L, Zhou Y, Wang D, Dou S (2020) Graphene-based composites for electrochemical energy storage. Energy Storage Mater 24:22–51
15. Zhang J, Zhang C, Li W, Guo Q, Gao H, You Y, Li Y, Cui Z, Jiang KC, Long H, Zhang D, Xin S (2018) Nitrogen-doped perovskite as a bifunctional cathode catalyst for rechargeable lithium-oxygen batteries. Appl Mater Interfaces 10(6):5543–5550
16. Xu C, Zhou J, Fu X, Zhang Y, Huang L (2018) Preparation and characterization of porous Ni-Mo alloy and its electrocatalytic performance for hydrogen evolution in filter-press type electrolyzer. Ionics 24(8):2399–2409
17. Liu A, Gao M, Ren X, Meng F, Yang Y, Gao L, Yang Q, Ma T (2020) Current progress in electrocatalytic carbon dioxide reduction to fuels on heterogeneous catalysts. J Mater Chem A 8:3541–3562. https://doi.org/10.1039/C9TA11966C
18. Ishihara T, Jang IC, Ida S (2019) Preparation of MnO_2-Cr_2O_3 mesoporous oxide and its application for an active and reversible air catalyst for Li-O_2 batteries. Electrochim Acta 317:594–603
19. Wang J, Li H, Xu N, Qiao J (2018) Optimization of rechargeable zinc-air battery with Co3O4/MnO2/CNT bifunctional catalyst: effects of catalyst loading, binder content, and spraying area. Ionics 24(12):3877–3887
20. Sun N, Liu H, Yu Z, Zheng Z, Shao C (2016) The electrochemical performance of $La_{0.6}Sr_{0.4}Co_{1-x}NixO_3$ perovskite catalysts for Li-O_2 batteries. Ionics 22:869–876
21. Kim JG, Kim Y, Noh Y, Lee S, Kim Y, Kim WB (2018) Bifunctional hybrid catalysts with perovskite $LaCo_{0.8}Fe_{0.2}O_3$ nanowires and reduced graphene oxide sheets for an efficient Li-O_2 battery cathode. ACS Appl Mater Interfaces 10(6):5429–5439
22. Kim J, Kang J (2019) An efficient electrocatalyst of NiO supported on carbon paper for nonaqueous Li-O_2 batteries. Ionics 25:5611–5616
23. Li Z, Ganapathy S, Xu Y, Zhu Q, Chen W, Kochetkov I, George C, Nazar LF, Wagemaker M (2018) Fe_2O_3 nanoparticle seed catalysts enhance cyclability on deep (dis)charge in aprotic Li-O_2 batteries. Adv Energy Mater 8(18):1703513
24. Yang S, Gen C, Zheng C (2018) Effective regeneration of $LiCoO_2$ from spent lithium-ion batteries: a direct approach towards high-performance active particles. Green Chem 20(4):851–862
25. Miao R, Tao B, Miao F, Zang Y, Shi C, Zhu L, Chu PK (2019) Co_3O_4 and $Co(OH)_2$ loaded graphene on Ni foam for high-performance supercapacitor electrode. Ionics 25:1783–1792
26. Shen C, Wen Z, Wang F, Wu T, Wu X (2016) Cobalt-metal-based cathode for lithium-oxygen battery with improved electrochemical performance. ACS Catal 6(7):4149–4153
27. Hyun S, Shanmugam S (2017) Mesoporous Co-CoO/N-CNR nanostructures as high-performance air cathode for lithium-oxygen batteries. J Power Sources 354:48–56

28. Hao Y, Xu Y, Liu W, Sun X (2018) Co/CoP embedded in a hairy nitrogen-doped carbon polyhedron as an advanced tri-functional electrocatalyst. Mater Horiz 5(1):108–115
29. Zhang M, Dai Q, Zheng H, Chen M, Dai L (2018) Novel MOF-derived Co@N-C bifunctional catalysts for highly efficient Zn-air batteries and water splitting. Adv Mater 30(10):1705431
30. Chen Y, Ni D, Yang X, Liu C, Yin J, Cai K (2018) Microwave-assisted synthesis of honeycomblike hierarchical spherical Zn-doped Ni-MOF as a high-performance battery-type supercapacitor electrode material. Electrochim Acta 278:114–123
31. Sharma N, Szunerits S, Boukherroub R, Ye R, Melinte S, Thotiyl MO, Ogale SB (2019) A dual-ligand Fe-MOF based robust high capacity Li ion battery anode and its use in a flexible battery format for electro-thermal heating. ACS Appl Energy Mater 2(6):4450–4457
32. Li W, Hu S, Luo X, Li Z, Sun X, Li M, Liu F, Yu Y (2017) Confined amorphous red phosphorus in MOF-derived N-doped microporous carbon as a superior anode for sodium-ion battery. Adv Mater 29(16):1605820
33. Combelles C, Doublet ML (2008) Structural, magnetic and redox properties of a new cathode material for Li-ion batteries: the iron-based metal organic framework. Ionics 14(4):279–283
34. Chen H, Xiao Y, Chen C, Yang J, Gao C, Chen Y, Wu J, Shen Y, Zhang W, Li S, Huo F, Zheng B (2019) Conductive MOF-modified separator for mitigating the shuttle effect of lithium-sulfur battery through a filtration method. Appl Mater Interfaces 11(12):11459–11465
35. Song MJ, Kim IT, Kim YB, Kim J, Shin MW (2017) Metal-organic frameworks-derived porous carbon/Co_3O_4 composites for rechargeable lithium-oxygen batteries. Electrochim Acta 230:73–80
36. Lang X, Ge F, Cai K, Li L, Wang Q, Zhang Q (2019) A novel Mn_3O_4/MnO nano spherical transition metal compound prepared by vacuum direct current arc method as bi-functional catalyst for lithium-oxygen battery with excellent electrochemical performances. J Alloys Compd 770:451–457