I have duly acknowledged all the sources of information which have been used in the thesis. This thesis has also not been submitted for any degree in any university previously. The content of the thesis has been partly published in

Abstract

Lithium-oxygen battery is a promising candidate for next-generation electric vehicle due to its high capacity. Yet its performance is still greatly limited by several disadvantages, including high overpotential and short cycling life etc. Consequently, cathode catalyst is required to improve the performance. In this project, CoMoO$_4$ porous nanorods were synthesized via a solvothermal method and their application in lithium-oxygen battery was investigated. The unique porous structure of CoMoO$_4$ porous nanorods is beneficial to the permeation of electrolyte and transportation of lithium ions, thus the lithium-oxygen battery with CoMoO$_4$ porous nanorods as the catalyst exhibited increased specific discharge capacity (4680 mAh/g), lower charge potential and longer cycling life (41 cycles at 500 mAh/g capacity limit).
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Part 1. Introduction

Due to the energy crisis and environmental issues caused by fossil fuels, there is an exigent demand of green energy resources to maintain the functioning of the society with less influence to the environment. Battery is one of the most promising resources since it is portable and has no memory effect. Up to now, lithium-ion battery has been widely applied in common portable electric devices such as digital watches, cell phones and laptops. Recently, electric vehicles using lithium-ion battery as power resource have also been commercialized. However, as the specific energy is restricted by the reaction mechanism, the application of lithium-ion battery in larger machinery remains unsuccessful [1-3].

To solve this problem, many new types of batteries such as lithium-sulfur battery and lithium-oxygen battery were fabricated. Among them, only lithium-oxygen battery possesses the theoretical and actual specific energy capacities (Figure 1.1) that can be compared with the traditional fossil fuels. The theoretical specific energy capacity of lithium-oxygen battery is over 10000 Wh/kg, which is much higher than that of lithium-ion battery. For actual performance, the maximum capacity of lithium-oxygen battery could easily reach 3000 Wh/kg, while the actual performance of lithium-ion battery is only about 200 Wh/kg [4-7]. Thus lithium-oxygen battery is of great interest in recent years.

![Figure 1.1 Specific energy capacities of various batteries. Reprinted from ref. 2 with permissions from John Wiley and Sons, Copyright 2011.](image-url)
1.1 Architecture of lithium-oxygen battery

The basic components of lithium-oxygen battery include porous air cathode, electrolyte and pure lithium anode. Based on the types of electrolyte, lithium-oxygen battery is classified into three types, including aprotic, aqueous and solid-state cells as shown in Figure 1.2 [8]. Besides, mixed aqueous/aprotic type with aqueous cathode and aprotic anode has also been realized. Due to the better cycling performance and relatively higher specific capacity, the aprotic type receives extensive attentions compared with other three types. Therefore the focus of this project is on aprotic lithium-oxygen battery. The separators are commonly employed to store aprotic electrolytes and prevent the direct contact between electrodes. [9]

![Figure 1.2 Schematic structures of various Lithium-oxygen Batteries, (a) with nonaqueous electrolytes, (b) with hybrid electrolytes and (c) with all solid-state electrolytes. Reprinted from ref. 8 with permission from the ChemPlusChem, Copyright 2015.](image)

1.2 Mechanism

Li$_2$O$_2$ has been identified as the cycling product. As shown in Figure 1-3, during discharge, oxygen taken from outside atmosphere is reduced at the porous cathode, then combines with lithium ion to form the final discharge product Li$_2$O$_2$ (oxygen reduction reaction, ORR). During charge, Li$_2$O$_2$ is electrochemically decomposed, (oxygen evolution reaction, OER). Despite the reversibility has been proved, there are some arguments about the real working mechanism. One of the most widely accepted models is shown below:
Discharge (ORR)
\[ \text{O}_2 + \text{Li}^+ + \text{e}^- \rightarrow \text{LiO}_2 \quad (E_0=3.0 \text{ V}) \]
\[ 2\text{LiO}_2 \rightarrow \text{Li}_2\text{O}_2 + \text{O}_2 \]
\[ \text{LiO}_2 + \text{Li}^+ + \text{e}^- \rightarrow \text{Li}_2\text{O}_2 \quad (E_0=2.96 \text{ V}) \]

Charge (OER)
\[ \text{Li}_2\text{O}_2 \rightarrow 2\text{Li}^+ + \text{O}_2 + 2\text{e}^- \]

As oxygen is not stored inside the battery, and the anode is made of pure lithium (rather than lithium compounds) which avoids the extra weight increase from other elements, the weight of the battery is greatly reduced and consequently the specific energy capacity increased \[^{10-11}\]. During discharge process, as shown in Figure 1.3, \text{Li}^+ is formed at the anode and transferred to the cathode. Then the reduced oxygen reacts with \text{Li}^+ and \text{Li}_2\text{O}_2 is formed at the interface between electrolyte and cathode. For the charging process, \text{Li}_2\text{O}_2 decomposed back to \text{Li} and oxygen \[^9\].

![Figure 1.3 Reacting mechanism of aprotic lithium-oxygen battery. Reprinted from ref. 9 with permission from the American Chemical Society, Copyright 2014.](image)

\text{LiO}_2 may further react with oxygen to form the final products or function as discharge product as well as shown in Figure 1.4 \[^{12}\]. It is also proved that \text{O}_2\text{ }^2^- appears during the reactions and lead to side reactions with carbon component in the cell \[^{13}\].
Figure 1.4 Reaction mechanisms that using Li$_2$O and LiO$_2$ as discharge product with presence of (a) 15-atom silver cluster (b) 3-atom silver cluster. Reprinted from ref.12 with permission from Nature Publishing Group, Copyright 2017.

1.3 Challenges and Solutions

Although the energy capacity of lithium-oxygen battery is promising, several shortages greatly limit its actual performance. The practical specific energy capacity is indeed much higher than that of lithium-ion battery. However, it is still not satisfactory comparing with the theoretical values. Besides, the cycling performance of lithium oxygen battery is far poorer than lithium-ion battery, with the latter can stably operates for at least 1000 cycles. Lithium-oxygen battery suffers from high charge overpotential issues due to the insolating and insoluble nature of Li$_2$O$_2$. Poor stability of cathode and electrolyte and anode may also lead to the poor performance$^{[14]}$. Furthermore, although the lithium-oxygen batteries are expected to be able to work in air, the disturbance from CO$_2$ and water vapor would greatly jeopardize the stability of the components and lead to various side reactions$^{[15]}$. To solve these shortages, several solutions and mechanisms have been proposed.
The decomposition mechanism of Li$_2$O$_2$ during charging process was explored, and the result indicated that the decomposition voltage was greatly dominated by the crystallinity. Amorphous Li$_2$O$_2$ is easier to be decomposed compared with bulk Li$_2$O$_2$ crystal$^{[16]}$.

In order to prevent the decomposition of anode due to water vapor, a hydrophobic thin film that allows the transportation of lithium ions is coated over the anode. For example, Wu et al. successfully synthesized SiO$_2$ based super-hydrophobic quasi-liquid matrix serving as both the catalyst and hydrophobic coating (Figure 1.5), and it was proved to be rather effective in promoting the performance of the battery in humid atmosphere$^{[15]}$.

![Figure 1.5 Schematic plot of lithium-oxygen battery with SiO$_2$-based super-hydrophilic quasi-liquid matrix operating in humid atmosphere. Reprinted from ref.15 with permission from Royal Society of Chemistry, Copyright 2017.](image)

To reduce the decomposition of electrolyte during battery operation, it is required that the electrolyte must be stable at the operation voltage window of the battery, inert to lithium metal and lithium salt, able to rapidly diffuse oxygen and quickly transfer lithium ion. Moreover, the electrolyte must be able to endure nucleophilic attack during charging and discharging process$^{[17]}$. Different types of electrolytes were tested, but the electrolytes that exhibit the best performance are basically lithium salts dissolved in organic solvent. Based on the experience of lithium-ion battery design, carbonate-based electrolyte was chosen at the beginning. However, though it showed superior columbic efficiency$^{[17-19]}$, carbonate-based electrolyte was found to be reactive with superoxide anion O$_2^-$ that appears during the discharge process, resulting in the formation of undesired carbonate-based species rather than
reversely decomposable discharge products. This would lead to the production of CO$_2$ gas, rather than O$_2$ [20-22]. Ether-based electrolyte possesses better stability when contact with cathode and superoxide ions during discharge process [22, 23]. Though slow decomposition can still be observed [24], solutions such as adding with steric hindrance were found to be effective. Dimethyl sulfoxide (DMSO) based electrolytes are also of great interest because of its excellent stability, specific energy, lithium ion conductivity, oxygen diffusion ability, and discharge voltage [25, 26]. However, the low columbic efficiency and comparatively poor cycling life of this electrolyte greatly harmed its performance [20-22]. It was found by Togasaki et al that the types and concentration of dissolved lithium salts could affect the performance, and by optimizing these two factors, the property of DMSO based electrolyte could be greatly improved [8]. Due to the comparatively better performance, ether based and DMSO based electrolytes, they are widely used for research purpose.

Modification on cathode is another widely explored aspect. Cathodes of lithium-oxygen batteries are in general composed of substrate, binder, conductive carbon and catalyst. Substrate is simply function as the support of cathode material and provides conductivity. Carbon paper and nickel foam are commonly employed as substrate. To tightly combine the cathode material with the substrate, binders such as polyvinylidene fluoride (PVDF) and polytetrafluoroethlyene (PTFE) are always added. However, the binders are in general lack of flexibility and unstable at high temperature [27-29]. More importantly, the conductivity of the binders is far poorer than the cathode material [30]. Therefore, the development of new type binders and binder-free cathode is important. Recently, Zhong et al. produced a graphene based binder-free cathode that can not only operate in pure oxygen with prominent specific capacity and cycling life, but also perform quite well in ambient air due to the moisture-resistance characteristics of the cathode [31]. Yet this method can only be applied to limited types of cathode material.

Despite the significant improvement of the performance by the previously stated methods, cathode catalyst is still one of the simplest and most influential options to simultaneously solve the above problems because of its
unexceptional effect on lessening over-potential, altering Li$_2$O$_2$ crystallinity, enhancing the stability of the battery components and promoting the rate performance.

1.4 Catalyst

Carbon materials are one of the most popular choice for cathode material due to their abundance, high conductivity, extremely light weight and various forms that can provide sufficient specific surface area $^{[32-34]}$. Moreover, carbon is an effective catalyst for oxygen reduction reaction in discharge process $^{[35]}$. For the most common commercial carbon materials, such as carbon black and graphene, the high reactivity would result in the more byproducts, shorter cycling life and much lower specific capacity. Therefore, special structures or treatments are required. Pore size distribution and specific surface area of the carbon material has been proven to be influential to the battery performance $^{[36]}$. Based on this conclusion, many kinds of carbon materials with special micro-structures were explored. For example, one dimensional carbon nanostructure is one of the promising materials, due to its comparatively larger specific surface area and the availability to create porous structure $^{[36-38]}$. Lim et al successfully synthesized a hierarchical carbon cathode with aligned carbon nanotubes (CNTs) forming well-controlled porous structure, which also exhibited improved performance $^{[37]}$. Two-dimensional (2-D) materials such as hierarchical functional graphene nano-sheets were found to reach a high specific capacity as well $^{[39]}$. An ordered three-dimensional mesoporous/macroporous carbon sphere array was also found to enable better cycling performance $^{[40]}$. However, carbon is lack of catalytic activity for oxygen evolution reactions (OER) and thus catalysts that is active to OER (charging process) is mixed with carbon to provide better performances.

Consequently, noble metals and noble metal oxides are the most promising choices. Jeong et al tested Pt, Pd and Ru nanoparticles loaded on reduced graphene oxide (rGO) cathodes $^{[41]}$. All three types of metals exhibited outstanding catalytic activity on reducing over-potential, which confirmed the expectation based on the general performance of noble metals in oxygen
evolution reactions. Ru-incorporated carbon cathode showed the best performance of cycling life and over-potential in this system. Besides the overpotential, noble metal such as silver may also affect discharge product. Despite of the unexceptional performance in reducing over-potential and modifying discharge product, noble metals are not suitable for the application in Li-O₂ battery system. Other than the costing, the specific capacity would be sacrificed due to the weight of noble metals. Moreover, the nonselective catalytic activity could not only facilitate the decomposition of Li₂O₂, but also promote the decomposition of the electrolyte.

![Figure 1.6](image)

Figure 1.6 (a) First cycle of battery performance of rGO, Pt-rGO hybrid, Pd-rGO hybrid and Ru-rGO hybrid cell (b) Cycle performance of Pt-rGO hybrid cell (c) Pd-rGO hybrid cell and (d) Ru-rGO hybrid cell. Reprinted from ref. 41 with permission from American Chemical Society. Copyright 2015.

Non-precious metals are also tested as the cathode catalyst. Ren et al reported that the cell with CuFe/C exhibited lower overpotential and much better high rate performance. Though the cost is greatly reduced, the specific energy capacity of the non-precious metals is still lower than expectation due to the same problem as precious metals. Consequently non-precious metal oxides are considered as better options because of their abundance and weight. One of the most widely explored non-precious metal oxide types is perovskite oxide,
which is in the form of \( \text{XII} \text{A}^{2+} \text{VI} \text{B}^{4+} \text{O}^{2−}_3 \) or \( \text{XII} \text{A}^{2+} \text{VI} \text{B}^{4+} \text{O}^{2−}_4 \), including \( \text{CaTiO}_3 \) and \( \text{Ba}_2\text{TiO}_4 \) etc. Before being tested as the cathode catalyst, perovskite oxide was proved to be effective in catalyzing the oxygen evolution reactions and oxygen reduction reactions \([44-46]\). One of the most remarkable works is that the perovskite-based porous \( \text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3 \) nanotubes was found exhibiting excellent electro-catalytic activity \([47]\). Besides the rather low over-potential of 4V, the cycling life of the battery with \( \text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3 \) was three times longer than that of pure carbon cell. Various perovskite oxides have been attempted and their electro-catalytic effect can be generally observed \([48,49]\). Similar catalytic activity can also be predicted from the performance of simple metal oxides including \( \text{Co}_3\text{O}_4 \) \([50]\) and \( \text{MnO}_2 \) \([51]\). Besides, transition metal oxides such as \( \text{NiCo}_2\text{O}_4 \) \([52]\), \( \text{NiFe}_2\text{O}_3 \) \([53]\) and \( \text{CuCo}_2\text{O}_4 \) \([54]\) have also been explored. However, metal oxides are generally insulating and of much lower specific energy densities. Similar to pure metal catalysts, the maximum specific energy capacity may still be compromised.

To compensate the less ideal electro-catalytic activity and further promote the permeation of electrolyte and transport of lithium ions, porous and nanostructured materials are widely employed in order to increase specific surface area and consequently provide more active sites. Besides, higher energy density of the catalyst could also lower the negative effect on specific capacity. Among the mixed transition metal oxides, \( \text{CoMoO}_4 \) nanomaterial is considered a good candidate for cathode catalyst due to its stability in alkaline media \([55]\), comparatively higher specific capacity \([56]\) and effectiveness to catalyze oxygen evolution reaction \([55]\). Although \( \text{CoMoO}_4 \) has been tested in several electric devices including supercapacitors \([57]\) and lithium-ion batteries \([58]\), its electro-catalytic activity in lithium-oxygen battery has not been tested yet. Therefore it is meaningful to examine the performance of lithium-oxygen battery with \( \text{CoMoO}_4 \) loaded on the cathode. In this work, high specific surface area \( \text{CoMoO}_4 \) porous nanorods were synthesized via a solvothermal method, and they were loaded on the cathode of lithium-oxygen battery serving as the electro-catalyst. The experimental results reveal that the battery exhibited prominent performance, and the \( \text{CoMoO}_4 \) porous nanorods possess bi-functional electro-catalytic activity.
Part 2. Methodology

2.1 Synthesize of CoMoO$_4$ porous nanorods

The CoMoO$_4$ precursor was prepared by hydrothermal method. Firstly 0.5 mmol Na$_2$MoO$_2$·2H$_2$O and 0.5 mmol Co(NO$_3$)$_2$·6H$_2$O were dissolved in the mixture of ethanol, ethylene glycol and deionized water with volume ratio of 2:1:2, and was constantly stirred for over 5 h with magnetic stir to ensure uniform solution. Secondly the solution was transferred into a Teflon lined stainless steel autoclave and heated at 180 °C for 6 h. The autoclave was cooled to room temperature naturally afterwards. Thirdly the resultant product was recovered by centrifugation. Ethanol, acetone and deionized water were used to wash the product in order to remove the impurities. Finally, the precursor was dried at 80 °C and then annealed in argon at 400 °C for 6 h, thus CoMoO$_4$ porous nanorods were obtained.

2.2 Material Characterization

X-ray diffraction (XRD) patterns of the samples were recorded with a Bruker D8-Advance X-ray diffractometer with Cu K$_\alpha$ radiation of wavelength 0.15406 nm. Scanning electron microscope (SEM), transmission electron microscope (TEM), scanning transmission electron microscope (STEM) and field emission scanning electron microscope (FESEM, JEOL JSM 6700F) were used to examine the morphology. To determine the Brunauer-Emmett-Teller (BET) surface area of the samples, nitrogen adsorption isotherms were recorded at 77 K on a surface area & pore size analyzer. The pore size distribution was calculated according the Barrett–Joyner–Halenda (BJH) method. Thermogravimetric analysis (TGA) was performed by a TA instrument 2960 in nitrogen atmosphere, with the heating rate of 10 °C/min from room
temperature to 900 °C. X-ray photonelectron spectroscopy (XPS) spectrum peaks were calibrated with respect to C 1s peak of carbon (284.6 eV). Raman spectrum was collected on Renishaw inVia 2000 with the excitation laser of 532 nm. To examine the electrode morphology after discharge and charge processes, the electrodes were dissembled, rinsed with acetonitrile and dried in glove box at room temperature for characterization.

2.3 Lithium-oxygen Battery Assembly

The structure of a coin-cell type lithium-oxygen battery employed for this project is shown in Figure 2.2. The cathode was fabricated from the mixture of CoMoO$_4$, Vulcan XC-72 (VX-72) and polyvinylidene fluoride (PVDF, act as binder) with mass ratio of 5:4:1 dispersed in Nmethyl-2-pyrrolidone (NMP). The composite was coated on the diffusion layer collector (Toray Carbon Paper) and dried at 100 °C for at least 12 h. The mass loading of the cathode may vary slightly and the typical value was 0.7~1.0 mg/cm$^2$. To make a comparison, pure carbon cathode was also prepared with VX-72 and polyvinylidene fluriode (PVDF) with mass ratio of 9:1 dispersed in NMP following the same procedure.

The assembly of the coin-cell type battery was conducted in a glove box in argon atmosphere. The sequence of the cell component is shown in Figure 2.2. The surface coated with CoMoO$_4$ and VX-72 was in contact with the separator. Glass fiber was used to separate cathode and anode. The selected electrolyte was 0.1 M lithium perchlorate (LiClO$_4$) in dimethyl sulfoxide (DMSO), and both the cathode and separator were soaked with the electrolyte to guarantee its fully permeation. The lithium anode is assembled at the other side of separator. Spacer and disk spring were used to ensure the tight packing of the battery in order to reduce inner resistance. Extra care should be taken to ensure all the components were centered without touch the cell case to prevent possible short circuit.
Finally, the as-fabricated battery was transferred into a self-made pressure-tight glass container (Figure 2.3). The weight of the cathodes were measured and labeled on the container for further calculation. The Argon inside the container was replaced with oxygen afterwards.
2.4 **Battery Performance**

The discharge/charge cycling curves were recorded on a LAND multichannel battery performance testing system, and the specific capacity was calculated based on the total mass of the electrode. For the galvanostatic discharge/charge test, the voltage window was set to be 2~4.5 V, and the current densities used were 0.04 mA/cm\(^2\), 0.08 mA/cm\(^2\), 0.16 mA/cm\(^2\) and 0.24 mA/cm\(^2\) to examine the over-potential, maximum discharge capacity and the rate performance. For the cycling performance test, the cut-off capacity was set as 500 mAh/g.
Part 3. Results and Discussions

3.1 Characterization of the As-prepared Sample

The precursor used for preparing CoMoO$_4$ was characterized by XRD and SEM, and the results are shown in Figure 3.1. It can be observed that the precursor was composed of nanorods with diameter of 30~60 nm and length of up to 600 nm. The peaks of the XRD pattern are assigned to hydrate CoMoO$_4$, rather than CoMoO$_4$ (PDF#14-0087 and PDF#26-0477).

![XRD pattern and SEM image of the precursor.](image)

The composition of the precursor can be further confirmed by the TGA analysis result. On the TGA curve shown in Figure 3.2, three distinct weight losses can be observed. The first continuous weight loss occurred below 100 °C indicates the evaporation of water adsorbed on the surface. The second weight loss occurred between 200~300 °C, which can be attributed to the dissociation of crystalliferous water in the hydrate CoMoO$_4$. The third weight lose can be assigned to the conversion from CoMoO$_4$ hydrate form to CoMoO$_4$ phase by releasing of the remaining water.$^{[59-60]}$
Figure 3.2 TGA curve of the precursor.

Figure 3.3(a) shows the XRD pattern of the as-prepared CoMoO$_4$ sample. The sharp and strong peak in this pattern can be well assigned to the monoclinic CoMoO$_4$ phase (PDF #21-0868). On the other hand, several distinct bands at 336, 364, 696, 811, 871 and 934 cm$^{-1}$ appeared in the Raman spectrum shown in Figure 3.3(b), which can be attributed to the characteristic vibrations of CoMoO$_4$[58,61]. These results verify that the water molecules in the precursor can be removed by the annealing process and the final product is CoMoO$_4$.

Figure 3.3 (a) XRD pattern and (b) Raman spectrum of the as-prepared sample.

Both the SEM and TEM images shown in Figure 3.4 (a) and (b) indicate that the CoMoO$_4$ sample is constituted by CoMoO$_4$ nanorods with the similar size as the precursor. The lattice fringe with distance of 0.67 nm can be observed in the HRTEM image shown in the inset of Figure 3.4 (b), which is corresponding to the (001) plane of CoMoO$_4$. The SEM image in Figure 3.4 (c) reveals that the nanorods are porous in nature. This observation confirms
that CoMoO$_4$ porous structure can be obtained by using a mixed-solvent solvothermal synthesis route.

Figure 3.4 (a) SEM, (b) TEM, HRTEM (inset) and (c) STEM images of CoMoO$_4$ sample.

The specific surface area and pore size distribution of the sample are determined by the nitrogen adsorption-desorption isotherms. From the curve shown in Figure 3.5, the specific surface area of porous CoMoO$_4$ nanorods is calculated to be 39 m$^2$/g, obviously larger than those of nanoparticles [63], nanofibers [61], nanorods [64], nanoplates and submicron particles [63]. Just as indicated by Figure 3.4(c), the CoMoO$_4$ nanorods possess porous structure, thus the pore size distribution was also calculated and the result is presented as the inset in Figure 3.5. According to Sun et al [62], such a porous structure is beneficial to promote the permeation of electrolyte and transfer of lithium ions, which can further enhance the catalytic activity and improve the performance of the battery.

Figure 3.5. Nitrogen adsorption–desorption isotherms of as-prepared CoMoO$_4$ and the pore size distribution curve (inset).
Furthermore, XPS spectrum was used to analyze the composition and chemical bonds in the sample. In Figure 3.6(a), two clear peaks located at 780.4 eV and 796 eV and the corresponding shakeup satellite peaks (marked as Sat. in the Figure) can be observed on the Co spectrum, which are characteristic peaks of Co 2p and Co$^{2+}$ respectively $^{[65,66]}$. Besides, two peaks at 232.5 eV and 235.4 eV are also observed on the Mo XPS spectrum shown in Figure 3.6 (b), indicating that the valence state of Mo element in CoMoO$_4$ is +6 $^{[66]}$. The spectrum of oxygen in Figure 3.6 (c) exhibits a clear peak at 529.2 eV, which reveals a typical metal-oxygen bond $^{[67]}$. Thus, the valence state of Co, Mo and O in CoMoO$_4$ are +2, +6 and -2, respectively.

![XPS spectra of CoMoO$_4$ nanorods](image)

Figure 3.6 (a) Co, (b) Mo and (c) O XPS spectra of CoMoO$_4$ nanorods.

### 3.2 Battery Performance

To examining the catalytic efficiency of CoMoO$_4$ porous nanorods, a lithium-oxygen battery using CoMoO$_4$ nanorods loaded carbon as the cathode was assembled. The full discharge-charge curves of batteries using CoMoO$_4$ and pure carbon as the cathodes are shown in Figure 3.7(a), and the current density is 0.04 mA/cm$^2$. By comparing with that of pure carbon cathode battery, the maximum discharge capacity of CoMoO$_4$ cathode battery significantly increased. Namely, the maximum discharge capacity of latter is 4680 mAh/g, while that of the former is only 3787 mAh/g. However, the discharge potentials for both the batteries are the same (2.8 V), indicating a negligible electrocatalytic effect of CoMoO$_4$ to ORR process. This is mainly resulted from the prominent electrocatalytic activity of carbon to ORR process, and consequently CoMoO$_4$ have comparatively much less effect on discharge.
There are two plateaus at 3.7 V and 4.2 V during charging process. According to the previous reported results, the first plateau can be attributed to the decomposition of LiO$_2$-like species that happened at 3.5~3.8 V, and the second one can be ascribed to the oxidation of Li$_2$O$_2$ [68]. In comparison, such plateaus were not observed for the pure carbon cathode battery, which indicates that the presence CoMoO$_4$ is beneficial for the formation of LiO$_2$-like species. This conclusion also supported the claim of Wang et al [69]. Besides, the two plateaus of CoMoO$_4$ battery are lower than those of the pure carbon cathode battery, proving that CoMoO$_4$ possesses quite high electrocatalytic activity to the charging process.

For analyzing the rate characteristic of the batteries, the full discharge/charge performances were further tested with current densities of 0.08 mA/cm$^2$, 0.16 mA/cm$^2$ and 0.24 mA/cm$^2$. As shown in Figure 3.7(b), the maximum discharge capacity of 3583 mAh/g, 3111 mAh/g and 1908 mAh/g can be attained for the CoMoO$_4$ cathode battery, respectively.

![Figure 3.7(a)](image)

**Figure 3.7 (a)** The first cycle of full discharge/charge performance of CoMoO$_4$ cathode and pure carbon cathode batteries at current density of 0.04 mA/cm$^2$ (b) Rate performance of CoMoO$_4$ cathode battery.

Furthermore, the cycling performances of CoMoO$_4$ (Figure 3.8(a)) and pure carbon (Figure 3.8(b)) cathode batteries were obtained by the capacity-limited method [70]. For the CoMoO$_4$ cathode battery, 41 stable cycling operations can be reached, while only 18 cycles can be maintained for the pure carbon cathode battery before it broke down.
Figure 3.8 Cycling performance of (a) CoMoO$_4$ cathode and (d) pure carbon cathode batteries.

Figure 3.9 presents the first four full discharge/charge curves of CoMoO$_4$ cathode battery (Figure 3.9(a)) and pure carbon cathode battery (Figure 3.9(b)) at current density of 0.16 mA/cm$^2$. For each cycle, the overpotential of CoMoO$_4$ battery is clearly lower than that of pure carbon one. Moreover, the maximum capacity of CoMoO$_4$ battery can still retain 1365 mAh/g after four cycles, while the value of pure carbon battery is only 410 mAh/g. All these results verify that CoMoO$_4$ can effectively reduce the overpotential, increase the maximum capacity, enhance the stability of the battery and promote the rate performance at higher current density.

Figure 3.9 The first four full discharge/charge cycles of (a) CoMoO$_4$ and (b) pure carbon cathode batteries.
3.3 Reversibility

In order to test the reversibility of the batteries, morphology evolution of the CoMoO$_4$ cathode during the discharge-charge processes were examined by FESEM, XRD and XPS. The FESEM image clearly indicates that the surface of carbon paper substrate was covered with the mixture of carbon particles and CoMoO$_4$ nanorods at beginning (Figure 3.10 (a)). After the discharge process, a layer of thin-film like discharge product covered the original surface (Figure3.9 (b)), which was almost entirely removed after the charging process, and the cathode restored its original morphology (Figure 3.10 (c)). This phenomenon implies that most of the discharge products can be removed by recharging process.

![Figure 3.10 FESEM images of CoMoO$_4$ cathode at (a) pristine, (b) discharge and (c) recharge states.](image)

For further investigating the reactions happened on the surface of CoMoO$_4$ cathode during the charge/discharge processes, XRD and XPS are further used to examine the products. On the XRD pattern shown in Figure 3.11(a), two peaks of Li$_2$O$_2$ (denoted with asterisks) appeared after discharge, indicating that crystallite Li$_2$O$_2$ formed as the major discharge product [71]. These two peaks almost disappeared upon recharge, which reveals that Li$_2$O$_2$ decomposed in this process. Similar phenomenon can also be observed in the corresponding XPS spectra (Figure 3.11 (b)). A peak at 54.7 eV appeared after the discharge process indicating the appearance of Li$_2$O$_2$, and this peak became nearly neglectable after recharging. This phenomenon further confirms the reversibly of the CoMoO$_4$ cathode materials, and hence, the corresponding batteries.
Figure 3.11 (a) XRD patterns and (b) XPS spectra of the products formed on the cathode surface.
Part 4. Conclusion

In summary, porous CoMoO$_4$ nanorods were prepared and employed as cathode material. The porous structure of CoMoO$_4$ sample was induced by mixed solvent and could promote the permeation of electrolyte and the transfer of lithium ions, and consequently the rate of the cell can be enhanced. Porous CoMoO$_4$ nanorods exhibited excellent catalytic activity on both OER (lower charging potential) and ORR process (larger maximum discharge capacity) compared with bare VX-72 cell. Meanwhile, the CoMoO$_4$ cell can stably operate 41 cycles at 500mAh/g, which indicates an enhanced stability of cell component. Moreover, the lithium-oxygen cell with CoMoO$_4$ shows excellent rate performance when tested with different current density. These superior characteristics guaranteed its promising application in lithium-oxygen battery.
Part 5. Acknowledgement

I would like to express my sincere appreciation to A/P Chen Wei for giving me this valuable opportunity to work in his group and on this topic. I thank him for the encouragements and insightful suggestions given on not only this project, but also the plan of my future carrier. I truly learned a lot from him about what it takes to become a qualified researcher.

Special thanks also to my mentor, Mr. Wang Liangjun, for his guidance into this new field and his patience on teaching me the basic procedure of performing the experiments. Discussions with him greatly improved my understanding of lithium-oxygen battery system.

My gratitude extended to Dr. Lyu Zhiyang and Dr. Dong Wenhao for their helpful advice on this project. Their rich experiences also helped me avoid many common mistakes in paper writings.
Part 6. References


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