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Metal-oxygen bonds: stabilizing the intermediate species towards practical Li-air batteries

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Metal-oxygen bonds: stabilizing the intermediate species towards practical Li-air batteries

Abstract

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Metal-oxygen bonds: stabilizing the intermediate species towards practical Li-air batteries

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Abstract

Rechargeable nonaqueous Li-air batteries are attracting much attention due to their far higher theoretical energy density than lithium-ion batteries. However, Li-air batteries suffers from poor round-trip efficiency, low rate capability and poor cycle life. To reduce charge overpotentials by understanding reaction mechanism and to operate in ambient air instead of pure oxygen are prerequisites to realization of practical Li-air batteries. Here, we demonstrate a practical Li-air battery using $\text{Mo}_2\text{C}/\text{CNT}$ as a potential promoter with high round-trip efficiency ($\sim 80\%$) and improved cycling performance (40 cycles) because Mo_2C stabilizes the intermediate species from reduction of both O_2 and CO_2 . The stabilization via formation of Mo-O bonds prevents further reduction and disproportionation of intermediate species to generate crystalline Li_2O_2 and Li_2CO_3 , thus reducing the charge overpotentials normally caused by the decomposition of crystalline Li_2O_2 and Li_2CO_3 . In all, this work provides improved understanding of the general role of solid promoters and enables rational design of promoters towards practical Li-air batteries.

1. Introduction

The Li-air battery, as one of the most promising power sources for electric vehicles, has attracted increasing attention over the last decade, owing to its specific energy density, which is 3-5 times as high as that of the state-of-the-art lithium ion batteries [1,2]. Certain factors, however, such as sluggish reaction kinetics, chemical instability of electrolytes, and moisture susceptibility, act as major obstacles to the realization of practical Li-air batteries. One major challenge for the realization of the Li-air batteries is reducing large voltage hysteresis and thus improving low round-trip efficiency through a clear understanding of the reaction mechanism of the catalyst. Although numerous catalysts have been recently developed to reduce the large charge-discharge voltage gap to increase the energy efficiency [3-6], a better understanding of the detailed mechanisms of the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER) still requires further systematic investigation. Given the mechanism of discharge product growth and decomposition, it is somewhat hard to envision how electrocatalysis could actually occur. As is well known, electrocatalysis occurs when an active catalytic site lowers the barrier of the kinetic limiting step in the mechanism, but the catalytic site itself is not changed during the reaction. It is difficult to see, however, how Li_2O_2 and LiO_2 could have enough mobility for true catalysis to occur, owing to their insolubility in the electrolyte. There is no true electrocatalysis in the same way as is observed for aqueous ORR/OER, where soluble products are formed, but added nanoparticles could have some beneficial effects on the morphology and charge transport at higher currents and capacities [7]. If there were such particles, however, such as platinum on the surface of carbon, they would rapidly be covered up by solid Li_2O_2 or LiO_2 , and the dominant electrochemistry then becomes simply the Li- O_2 ORR on Li_2O_2 or LiO_2 . The material design which has been already successfully applied in aqueous ORR/OER needs to be changed, because the

intermediate product is soluble in aqueous electrolyte, which could not affect the catalytic sites of nanocatalyst particles.

Noble metal and transitions metal oxides have been extensively investigated as catalysts for Li-O₂ batteries, and several catalytic mechanisms have been proposed. Yao *et al.* proposed that enhancement of Li₂O₂ oxidation is mediated by chemical conversion of Li₂O₂ with slow oxidation kinetics to a lithium oxide [6]. Wang *et al.* proposed that partial oxidation of ruthenium catalyst can stabilize the highly unstable peroxide/superoxide that is caused by the lithium-deficient Li₂O₂ (or Li_{2-x}O₂), forming Li_{2-x}O₂(solid)-Ru at the interface [8]. Recently, a one-electron charge process in lithium oxygen batteries was observed, and it was reported to be responsible for low overpotential during the charge process. Lu *et al.* demonstrated that the LiO₂ formed in the Li-O₂ battery is stable enough so that the battery could be repeatedly charged and discharged with a very low charge potential, and they proposed that the intermetallic compound Ir₃Li and LiO₂ both have a similar orthorhombic lattice, so it may act as a template for the growth of crystalline LiO₂ [9]. Meanwhile, Trahey *et al.* proposed that MnO₂ can act as a “Li_xO_y-storage material”, reversibly storing lithium-oxide species during the Li-O₂ reactions, based on density functional theory (DFT) computations, and in this case, the transition metal oxides in lithium air batteries do not act as “catalyst” in the traditional sense of facilitating a chemical reaction while remaining unchanged, but actually undergo chemical and structural changes themselves as well [10]. All the above shows the synergetic effect between the catalyst and the intermediate discharge product Li_xO₂, which possibly can account for the reduced charge overpotential due to the solid-state reaction in the discharge process. Even though extensive studies have been conducted to elucidate the role of conventional solid catalysts, the operating mechanism remains elusive and controversial in Li-O₂ batteries.

The other major challenge to realize practical Li-air batteries is how to eliminate the influence of CO₂ and moisture when operate in ambient air. Supposing that moisture, which is known to fatally degrade electrolyte and lithium anode, is removed by an air dehydration membrane [11], CO₂ should have most influence on the chemistry of Li-air batteries among various constituents of air. Despite its low concentration in air, the high solubility of CO₂ in organic electrolytes results in the huge possibility of CO₂ being incorporated into battery reaction [12]. To exclusively investigate and understand the operating mechanism of CO₂, a rechargeable Li-CO₂ battery was proposed and extensively studied based on the reversible reaction of $4\text{Li} + 3\text{CO}_2 = 2\text{Li}_2\text{CO}_3 + \text{C}$ [13-18]. As a wide band-gap insulator and insoluble discharge product, Li₂CO₃ causes a high overpotential (> 4.0 V vs. Li/Li⁺) to decompose in charge.

Our previous studies have shown that Mo₂C/carbon nanotube (CNT) could stabilize CO₂ reduction intermediate to generate amorphous discharge product in discharge, avoiding ultimate formation of Li₂CO₃. The stabilized discharge product could decompose at low potentials (~ 3.5 V vs. Li/Li⁺) in charge, efficiently reducing charge overpotential and CO₂ evolution barrier in Li-CO₂ batteries [19]. Somewhat differently, it is still under debate whether Mo₂C can have any effect on charge and how Mo₂C improve oxygen evolution in Li-O₂ batteries. Kwak *et al.* demonstrated that Mo₂C could increase the electrical efficiency and improve the cycling performance of Li-O₂ batteries, owing to the formation of metallic non-crystalline MoO₃-like layers on the Mo₂C nanoparticle [20]. However, Kundu *et al.* observed white glass fiber separator changes to dark blue after several discharge-charge cycles, so they concluded the low charge potential of Mo₂C comes from the oxidation of Li_xMoO₃ [21]. In this report, we have demonstrated the improved electrochemical performance of the Li-O₂ battery using Mo₂C/CNT as promoter, and carried out essential electrochemical techniques, with analytical techniques such as X-ray powder diffraction

(XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and energy dispersive X-ray spectroscopy (EDS) to investigate the reaction mechanism of Mo₂C/CNT. Based on the presented data and as an extension for our previous Li-CO₂ battery studies, we proposed the mechanism that Mo₂C/CNT could efficiently stabilize the highly reactive LiO₂ to generate amorphous (Li-O-O)_x-Mo₂C as discharge product, thus preventing the formation of crystalline Li₂O₂, which is difficult to decompose and induces high overpotential during charge in Li-O₂ battery. We found that the stabilization of Mo-O bonds could prevent the formation of both crystalline Li₂O₂ and Li₂CO₃, so to maintain good cycling performance and high round-trip efficiency of Li-air batteries and Li-CO₂/O₂ batteries. These studies may offer insight and guidance of solid promoter design, and provide a feasible method for addressing major technical barriers to practical Li-air batteries.

2. Experimental Section

2.1. Synthesis of Mo₂C/CNT composite materials

Molybdenum carbide (Mo₂C)/carbon nanotube (CNT) composite materials were prepared via carbothermic reduction of a mixture of molybdenum trioxide (MoO₃) and CNTs. In a typical procedure, MoO₃ and CNTs were weighed according to the stoichiometric ratio based on the equation $2\text{MoO}_3 + 7\text{C} = \text{Mo}_2\text{C} + 6\text{CO}$ and mixed via ball milling for 24 h. The rotation speed was 300 rpm and the ball-to-powder weight ratio was 20:1. To protect the materials from oxidation, the milling jar was assembled in glovebox under high purity Ar atmosphere. After that, the mixture was heated at 950 °C for 1 h under Ar with a heating rate of 10 °C min⁻¹.

2.2. Preparation of batteries in different atmospheres

Mo₂C/CNT (or pure CNT) materials were mixed in N-methyl-2-pyrrolidone (NMP) liquid with a polyvinylidene fluoride binder (PVDF) with a weight ratio of active materials to PVDF of 8:2. The

slurry was pasted onto carbon paper disks (diameter of 14 mm) and dried for 12 hours at 120 °C under vacuum to remove the residual solvent. The loading of electrodes was ~4 mg. Electrochemical tests were carried out using coin cells composed of a lithium metal anode, electrolyte (1M LiCF₃SO₃ in tetraethylene glycol dimethyl ether (TEGDME) impregnated into a glass fiber separator (Whatman GF/D microfiber filter paper, 2.7 μm pore size)). All cell assembly procedures were carried out in an argon-filled glove box (oxygen and water contents less than 0.1 ppm). Li-O₂ battery tests were carried out in an O₂-filled chamber, and Li-air battery tests were carried out in an air-filled chamber with molecular sieves to reduce the moisture of ambient air. Li-CO₂/O₂ battery tests were carried out in an O₂/CO₂-filled chamber. Cells were left for 3 hours in this chamber for stabilization after filling the chamber with gas, but before testing.

2.3. Physical characterizations

Powder X-ray diffraction (XRD) was performed on a GBC MMA XRD ($\lambda = 1.54 \text{ \AA}$) with the voltage and current kept at -40 kV and 25 mA, respectively. Scanning electron microscopy (SEM) images were obtained from a JEOL JSM-7500FA field emission SEM, in which the accelerating voltage was set at 5.0 kV and the emission current was 10 mA. Raman spectroscopy was carried out on a Jobin-Yvon Horiba 800 with a 10 mW helium/neon laser at 632.81 nm excitation. Transmission electron microscopy (TEM) investigations were performed using a 200 kV JEOL ARM-200F instrument. Thermogravimetric analysis (TGA) was carried out in air using a Q500 (TA Instruments), with data analysis carried out using the Q Series software V. 2.5.0.255. The temperature range studied was from room temperature to 1000 °C at the rate of 10 °C min⁻¹. XPS measurements were performed on a VG Scientific ESCALAB 2201XL instrument configured with Al K α X-ray radiation. All spectra were fitted with Gaussian-Lorentzian functions and a Shirley-type background using CasaXPS software. For the analysis of Mo 3d spectra, constraints were

used on the fitting for component pairs: peak area ratio of 2:3 for $3d_{5/2}$: $3d_{3/2}$ and a maximum 0.2 eV difference in full width at half maximum (FWHM). The binding energy values were calibrated using the adventitious C 1s peak at 284.6 eV.

3. Results and Discussions

A schematic diagram depicting the preparation of $\text{Mo}_2\text{C}/\text{CNT}$ composites is shown in **Fig. 1a**, and the synthesis procedure at each step was also confirmed by SEM images (**Fig. 1b**). Bulk MoO_3 and CNTs were mixed via ball milling and calcinated. After calcination, the mixture of MoO_3 and CNT turned into uniformly distributed $\text{Mo}_2\text{C}/\text{CNT}$. MoO_3 was reduced by CNT, and bulk MoO_3 was transformed into Mo_2C nanoparticles, but unreacted CNT still existed and acted as the conductive skeleton for the composites. The final product was investigated by XRD (as shown in **Fig. 1c**), in which several typical diffraction peaks at 34.4° , 38.0° , 39.4° , 52.1° , 61.5° , 69.6° , and 74.6° were respectively assigned to the (002), (020), (211), (221), (203), (231), and (223) planes of β - Mo_2C (PDF-# 35-0787), confirming that MoO_3 was reduced to Mo_2C after thermal treatment. Thermogravimetric analysis (TGA) of the as-prepared $\text{Mo}_2\text{C}/\text{CNT}$ showed that weight ratio of residual CNT was 5.2 %, and the Mo_2C was determined to be 94.8% (Supplementary Information, **Fig. S1**). The high-resolution TEM (HRTEM) image indicates that the particles possess a typical crystalline texture, and the selected area electron diffraction (SAED) pattern of the as-prepared $\text{Mo}_2\text{C}/\text{CNT}$ shows (002), (100) rings of CNT and (002), (100) rings of Mo_2C , confirming the presence of carbon nanotubes and crystalline Mo_2C , which is in accordance with the XRD data (**Fig. 1d**). TEM images in a highly resolved small area of $\text{Mo}_2\text{C}/\text{CNT}$ show uniform distributions of Mo_2C and carbon nanotubes in both bright field and dark field, and energy dispersive spectroscopy (EDS) elemental mapping images in the same area show uniform distributions of Mo

and C elements (**Fig. 1e**). With all the above data, it was confirmed that Mo₂C/CNT was successfully synthesized.

The electrochemical testing was carried out using coin cells composed of a lithium metal anode, a glass fiber separator impregnated with electrolyte (1 M lithium triflate (LiCF₃SO₃) in tetraethylene glycol dimethyl ether (TEGDME)), and a cathode (loaded with CNT or Mo₂C/CNT on carbon paper). The reaction kinetics of Mo₂C/CNT was examined by cyclic voltammetry (CV) under oxygen and nitrogen between 2.0-4.2 V (vs. Li/Li⁺) at the scan rate of 0.1 mV s⁻¹. As shown in **Fig. 2a**, the cathodic peak of Mo₂C/CNT starts from 2.7 V (vs. Li/Li⁺), where the oxygen reduction reaction takes place in the cell, while half of the anodic peak starts from 3.3 V (vs. Li/Li⁺) where the deposited product starts to decompose. For comparison, there is no obvious peak under nitrogen, showing that the reaction is derived from the reduction of oxygen. The reversibility of Mo₂C/CNT under oxygen was tested at a cut-off capacity of 100 μ Ah at the current rate of 20 μ A, and the results showed that Mo₂C/CNT exhibits a remarkably low charging potential of 3.35 V, after 40 discharge-charge cycles (**Fig. 2b**). On the contrary, the current contributed by CNTs to the cathodic peak is relatively high, indicating that CNT has larger surface area and more active sites for oxygen reduction; but the current contributed by CNT to the anodic peak is low, indicating that the decomposition of discharge products cannot proceed well in this voltage range (**Fig. 2c**). In full discharge-charge tests, the potential gap for CNTs between discharge and charge is 1.67 V, but for Mo₂C/CNT, it is only 0.76 V, showing that the introduction of Mo₂C/CNT can significantly reduce charge overpotentials (**Fig. 2d**).

To investigate the cause of low charge voltage plateau, continuous galvanostatic discharge-charge was carried out in switched N₂/O₂ atmosphere (Supporting information, **Fig. S2**). In first step, after purging with oxygen, the cell using Mo₂C/CNT as electrode succeeded in discharging

and charging under oxygen for 20 hours. However, the cell failed in discharging when atmosphere was switched to N₂ in second step. In third step, the cell could resume discharging and charging for another 20 hours when atmosphere was switched to O₂. This study initially confirmed that the low charge voltage plateau is related to oxygen evolution reaction, not related to de-intercalation of lithium compound in same voltage range [22]. In a study performed by Kundu *et al*, they explained that the low charge voltage plateau derives from oxidation of Li_xMoO₃, and formation of Li_xMoO₃ gives a blue colour on glassfiber [21]. However, we found that such a deep blue colour on glassfiber could only be observed when the cell was overcharged under nitrogen. The glassfiber was clean after discharge and charge under oxygen, indicating the good reversibility can be maintained if voltage was limited below 3.8 V (Supporting information, **Fig. S3**). Based on this, we ascribed the deep blue colour to instability of Mo₂C at high voltage in place of the formation of Li_xMoO₃, and ascertained that the charge voltage should be limited below 3.8 V to avoid the reaction of Mo₂C.

In addition, Mo₂C/CNT electrodes at different stages were prepared and analyzed to obtain insight into the structural origins of the observed low charge potential and improved cycling performance. In a typical procedure, we assembled two Li-O₂ cells with Mo₂C/CNT as cathode, one was discharged to 2.0 V at the current rate of 20 μA, and after disassembly, we obtained the discharged electrode; the other was discharged to 2.0 V first, then charged to 3.8 V at the current rate of 20 μA, and after disassembly, we obtained the charged electrode. The pristine electrode is a freshly prepared Mo₂C/CNT electrode without any previous electrochemical testing. The voltage profile for electrode preparation is shown in **Fig. 3a**, and the pristine electrode, discharged electrode, and charged electrode were positioned at points A, B, and C in the voltage profile. We first used XRD to determine the structural changes of Mo₂C/CNT electrode during discharge-

charge process. As shown in **Fig. 3b**, the XRD patterns show peaks corresponding to Mo₂C and graphite from carbon paper in the pristine, discharged, and recharged Mo₂C/CNT cathodes, but there is no peak showing the presence of crystalline Li₂O₂ in the discharged Mo₂C/CNT electrode, indicating that an amorphous discharge product was formed during the discharge process. SEM was then used to confirm the existence of the amorphous discharge product, as shown in **Fig. 3c-e**. Uniformly dispersed Mo₂C and CNT were observed in the pristine Mo₂C/CNT electrode before discharge; after discharge, there is a thin film on the surface of the Mo₂C/CNT electrode, and then this thin film disappears after the electrode is fully charged.

To investigate this amorphous thin film on the surface of the Mo₂C/CNT electrode, X-ray photoelectron spectroscopy (XPS) of Mo 3d was carried out and fitted with the contributions of Mo²⁺, Mo³⁺, Mo⁵⁺, or Mo⁶⁺ on the surfaces of the Mo₂C/CNT electrodes (fitting details shown in the Supporting Information, **Table S1**). For the pristine Mo₂C/CNT electrode, the low oxidation states of Mo²⁺ and Mo³⁺ can be explained for the existence of both Mo-Mo and Mo-C bonds, and the high oxidation states of Mo⁵⁺ and Mo⁶⁺ can be explained for the contaminated surface of molybdenum oxides such as MoO₂ and MoO₃ when the Mo₂C/CNT was exposed in air (**Fig. 3f**). After discharge in oxygen, peaks for Mo²⁺ and Mo³⁺ disappeared while peaks for Mo⁵⁺ and Mo⁶⁺ increased, indicating the oxidation of Mo₂C surface with the formation of Mo-O bonds (**Fig. 3g**). After recharge in oxygen, peaks for Mo²⁺, Mo³⁺ recovered while peaks for Mo⁵⁺ and Mo⁶⁺ decreased to pristine state, indicating the reduction of oxidized Mo₂C surface with the cleavage of Mo-O bonds (**Fig. 3h**). Based on these results, the reversible formation and cleavage of Mo-O bonds may be responsible for the low charge overpotentials and high cyclability.

To corroborate the reversible formation and decomposition of the oxygen reduction product, we simultaneously characterized these different stages of Mo₂C/CNT electrodes by survey spectra of

XPS and EDS mapping. The survey spectra of XPS clearly reflect the change of oxygen peaks, showing deposition of oxygen species in discharge and releasing of oxygen species in charge (Supporting Information, **Fig. S4**). In agreement with the XPS results, the EDS element mapping clearly shows the change of intensity for elemental oxygen, indicating that reduction species of oxygen deposited on the surface of the Mo₂C/CNT electrode in discharge, and released from the surface of the Mo₂C/CNT electrode in charge (Supporting Information, **Fig. S5**). Moreover, when these electrodes were exposed to air for several days, crystalline Li₂MoO₄ was detected from discharged electrode only (Supporting Information, **Fig. S6**). This finding shows that amorphous discharge product has similar chemical property to mixed LiOH•H₂O and MoO₃ at room temperature [23], confirming the existence of Mo-O bonds in amorphous discharge product.

As mentioned above, Mo₂C does not operate as an electrocatalyst like Pt/C in the aqueous oxygen reduction reaction. Neither does it operate as an OER catalyst, decomposing crystalline Li₂O₂, which can normally be characterized by diffraction methods. Instead, it operates by a different mechanism that changes the pathway of O₂ reduction to insulating Li₂O₂, but stabilizes the reactive LiO₂ intermediate to form an amorphous product through solid-state reaction. In the absence of Mo₂C, reduction of O₂ to Li₂O₂ proceeds via the LiO₂ intermediate on the surface of CNT electrode during discharge [24]. Equation (1) shows the oxygen undergoes one-electron reduction to form O₂⁻, then combines with a Li⁺ ion to form LiO₂ in solution or surface adsorbed LiO₂ intermediate. Equation (2) and (3) show LiO₂ as a transient intermediate is not stable at room temperature and quickly converts to Li₂O₂ via a disproportionation reaction or an additional Li⁺-induced charge transfer. As a wide band-gap insulator and insoluble species, bulk Li₂O₂ is difficult to decompose below 4.0 V. Moreover, this highly oxidized LiO₂ intermediate could also induce the oxidization of the carbon surface to Li₂CO₃, and even one monolayer of Li₂CO₃ at the C-Li₂O₂

interface can cause a ~10-100-fold decrease in the exchange current density due to interfacial resistance to charge transport [25]. Unlike NaO₂ in Na-O₂ batteries, which generates and stably exists in the discharge stage and decomposes at low voltage plateau in the charge stage, the LiO₂ converts to Li₂O₂, which decomposes at high voltage above 4.0 V in the charge stage [26].

To capture and stabilize LiO₂ species could prevent them from surface-mediated disproportionation and further reduction to Li₂O₂. It is reported that Glassy carbon with surface defects, oxidized carbon and Ir-based catalyst were proved to stabilize Li_xO₂/LiO₂ species in discharge and facilely decompose in subsequent charge [9, 27, 28]. Unsaturated coordination of Mo states on the Mo₂C surface is thought to be responsible for its high catalytic activity towards dehydrogenation and electrochemical hydrogen evolution [12, 29]. Meanwhile, this metal center was expected to have a strong affinity for oxygen, thus favoring a surface mediated ORR process or CO₂ reduction process [19]. Moreover, the active surface is expected to be highly electrically conductive, owing to the well-known metallic properties of the underlying Mo₂C. Therefore, we speculate that Mo₂C could stabilize the active LiO₂ intermediate to generate amorphous (Li-O-O)_x-Mo₂C via the formation of Mo-O bonds, preventing further reduction and disproportionation of LiO₂ intermediate to crystalline Li₂O₂ in Equation (4). The facile decomposition of amorphous (Li-O-O)_x-Mo₂C in Equation (5), instead of difficult decomposition of crystalline Li₂O₂ may be responsible for the reduced charging overpotentials observed in our results.

This is also confirmed by the electrochemical behavior of Mo₂C/CNT in both O₂ and CO₂ in full discharge-charge testing (**Fig. 4a**). Different discharge voltage plateaus showed different reduction voltages based on the different electrochemical reduction of O₂ or CO₂. When the Mo in Mo₂C completes the coordination with O, regardless of whether the unsaturated Mo bonds with O from O₂ or CO₂, the Mo-O bond dissociation energy is the same, so the charge voltage plateau remains the same in both O₂ and CO₂ atmospheres. We also compared CNT and Mo₂C/CNT in cut-off capacity discharge-charge, and the Mo₂C/CNT prominently reduced the charge overpotential and improved the round-trip efficiency in both O₂ and CO₂ (**Fig. 4b**). At this point, we speculate that the formation of Mo-O bonds could stabilize the reduction intermediate with oxygen-containing groups. As shown in **Fig. 4c**, the reversible formation and decomposition of the amorphous discharge product in both O₂ and CO₂ via the formation and cleavage of Mo-O bonds in Li-O₂ batteries and Li-CO₂ batteries, make Mo₂C/CNT a potential efficient and CO₂-robust promoter in practical Li-air batteries.

Finally, we investigated the cycle stability of practical Li-air batteries using Mo₂C/CNT as electrode. After 5 discharge-charge cycling between the voltage of 2.0 V and 3.8 V, the capacity of practical Li-air battery using Mo₂C/CNT still maintain more than 80 %, with high energy efficiency of 80 % (**Fig. 5a**). In contrast, the capacity of practical Li-air battery using CNT shows fast fading to only 40 % after 5 discharge-charge cycling, with the charge voltage extend to 4.6 V (**Fig. 5b**). We also carried out cut-off capacity discharge-charge testing, and it was found that the Mo₂C/CNT can reversibly discharge and charge for 40 cycles (**Fig. 5c**) with high round-trip efficiency, showing good cycling performance even in presence of a trivial amount of CO₂.

To investigate the influence of CO₂, we increased the ratio of CO₂ by filling a mixture of CO₂ and O₂ which contained 50 % CO₂ instead of ambient air into the chamber. The cell using

Mo₂C/CNT can still reversibly discharge and charge for 40 cycles with round-trip efficiency of 80 % (**Fig. 5d**). Based on the low charge voltage plateau of ~ 3.4 V in both Li-air battery and Li-CO₂/O₂ battery, we exclude the formation of crystal Li₂O₂ and Li₂CO₃, which do not decompose until high voltage (> 4V vs. Li/Li⁺). At this point, our proposed mechanism was confirmed that the intermediate species from reduction of O₂ and CO₂ could be appropriately stabilized by Mo₂C/CNT promoter via the formation of Mo-O bonds. Since amorphous (Li-O-O)_x-Mo₂C and (Li-O-C-O)_x-Mo₂C generate instead of crystalline Li₂O₂ and Li₂CO₃ during discharge process, the subsequent decomposition could remain low charge voltage.

4. Conclusion

In summary, we have exploited Mo₂C/CNT as a promoter for practical Li-air batteries with high round-trip efficiency and good cycling performance. As a bifunctional promoter in both O₂ and CO₂ atmospheres, Mo₂C/CNT can efficiently stabilize both intermediate species from reduction of O₂ and CO₂ to generate amorphous (Li-O-O)_x-Mo₂C and (Li-O-C-O)_x-Mo₂C discharge product, respectively, preventing the formation of crystalline Li₂O₂ and Li₂CO₃. Correspondingly, the charge potential can be significantly reduced owing to decomposition of the amorphous discharge products, instead of the decomposition of crystalline Li₂O₂ and Li₂CO₃. Meanwhile, we predict that this promoter has the potential to pave the way towards a commercially achievable Li-air battery in an open system, not requiring a sealed oxygen tank. Our findings clearly identify the critical role of metal-oxygen bonds in Li-gas batteries, suggesting that the low valence metal in metal compound provides a suitable environment for surface stabilization of O₂ and CO₂ reduction product. This work has a broader implication to guide rational design strategies for other promoters such as metal carbides, metal sulfide which metal centers in the unsaturated coordination state. More importantly, the understanding of cationic redox and anionic redox further inspires us to

explore new battery systems with longer life and higher energy density such as anion redox metal compound/LiO_x system.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version.

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Fig. 1. a) Schematic illustrations depicting the synthesis procedure for $\text{Mo}_2\text{C}/\text{CNT}$ composite materials; b) SEM images of the synthesis procedure at each step; c) XRD pattern of $\text{Mo}_2\text{C}/\text{CNT}$ composites; d) transmission electron microscope (TEM) image with SAED pattern of the as-prepared $\text{Mo}_2\text{C}/\text{CNT}$; e) The corresponding bright field (BF) image, dark field (DF) image, and element mapping of $\text{Mo}_2\text{C}/\text{CNT}$ composite (green for C, and yellow for Mo)

Fig. 2. Electrochemical tests: a) Cyclic voltammograms of Mo₂C/CNT in oxygen and nitrogen; b) Galvanostatic discharge-charge voltage profiles of Mo₂C/CNT in oxygen for selected cycles; c) Cyclic voltammograms of Mo₂C/CNT and CNT in oxygen; d) Voltage profiles of the CNT and Mo₂C/CNT cathodes.

Fig. 3. a) Full discharge and charge cycle of Mo₂C/CNT in a Li-O₂ battery (pristine electrode at position A, fully discharged electrode at position B, and fully recharged electrode at position C). b) XRD images of Mo₂C/CNT electrode at different stages (pristine, discharged, recharged). c-e) SEM images of Mo₂C/CNT of Mo₂C/CNT electrode at different stages (pristine, discharged, recharged). f-h) XPS spectra showing Mo 3d peaks of Mo₂C/CNT electrode at different stages (pristine, discharged, recharged).

Fig. 4. a) Voltage profiles of Mo₂C/CNT as cathode in full discharge-charge for the Li-O₂ battery and the Li-CO₂ battery. b) Voltage profiles of Mo₂C/CNT as cathode in cut-off capacity discharge-charge for the Li-O₂ battery and the Li-CO₂ battery. c) Schematic illustration of the stabilization mechanism of Mo₂C/CNT in the Li-O₂ battery and the Li-CO₂ battery, showing the formation and cleavage of Mo-O bonds between Mo₂C and intermediate species from reduction of O₂ and CO₂ on discharge and charge.

Fig. 5. a) Voltage profiles of $\text{Mo}_2\text{C/CNT}$ in air for the first 5 cycles, with full discharge and recharge between 2.0 V and 3.8 V, at the current rate of 20 μA . b) Voltage profiles of CNT in air for the first 5 cycles, with full discharge and recharge between 2.0 V and 4.6 V, at the current rate of 20 μA . c) Voltage profiles for selected cycles of $\text{Mo}_2\text{C/CNT}$ in air, with a cut-off capacity of 100 μAh , at the current rate of 20 μA . d) Voltage profiles for selected cycles of $\text{Mo}_2\text{C/CNT}$ in CO_2/O_2 (1:1), with a cutoff capacity of 100 μAh , at the current rate of 20 μA .