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Graphic abstract

Performance-improved Li-O_2 battery with Ru nanoparticles supported on binder-free multi-walled carbon nanotube paper as cathode

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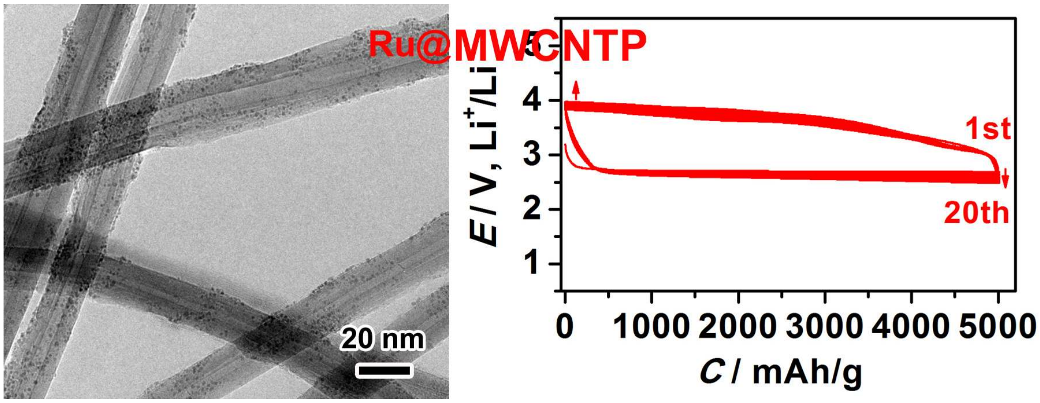
Ru nanoparticles supported on multi-walled carbon nanotube paper are applied as a cathode in Li-O_2 battery. The cathode can significantly reduce the charge overpotentials, and present a large discharge/charge capacity and stable cycles.



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ARTICLE TYPE

Performance-improved Li-O_2 battery with Ru nanoparticles supported on binder-free multi-walled carbon nanotube paper as cathode

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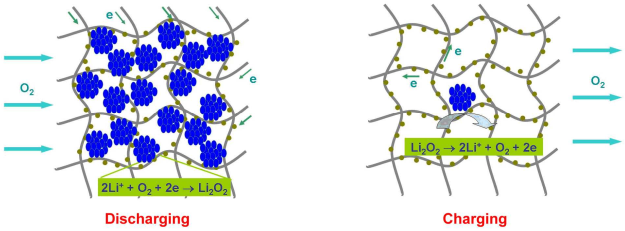
Ru nanoparticles have been deposited onto a multi-walled carbon nanotube paper (Ru@MWCNTP) via a wet chemical method. The resulting catalyst, Ru@MWCNTP has been demonstrated to significantly reduce the charge overpotentials of the Li-O_2 battery at a current density of 500 mA/g. The reversible formation and decomposition of Li_2O_2 can be revealed by X-ray diffraction (XRD). In the initial 20 cycles of discharge and charge, the Li-O_2 battery with Ru@MWCNTP presents a stable capacity of 5000 mAh/g and almost constant discharge/charge potentials, contrasting with the quickly decaying capacity of the bare MWCNTP without addition of Ru nanoparticles. The combination of porous networks of multi-walled carbon nanotubes (MWCNTs), beneficial for facile transport of both electrons and oxygen, and superior catalytic activity of Ru nanoparticles enables good cycling performance and rate capability of the Li-O_2 battery.

Li-O_2 batteries have been attracting intensive research attention, due to their potential large specific energy density.[1] The fundamental understandings and progress on Li-O_2 batteries have been obtained in the recent few years, while constructing a reversible Li-O_2 battery remains a difficult task.[2-8] This may be resulted from the facts: (i) lack of cycling-stable electrolytes, though glyme based electrolytes have been demonstrated to be the most relatively robust, and (ii) large overpotentials, specifically ~ 0.3 V in the discharging process that seems insensitive to the applied catalysts and ~ 1.0 V in the charging process.[2-11] Based on the relatively stable electrolytes, like dimethylsulfoxide (DMSO) and glyme based electrolytes, Li-O_2 batteries of either long cycles or large capacity have been reported.[12-18] However, the overpotential, especially in a charging process, is still large and can result in the instability of other cell components. For instance, carbon could be decomposed beyond a certain potential that depends on the carbon surface property and react with Li_2O_2, and possible decomposition of electrolytes occurs in the presence of Li_2O_2.[2-6] Reducing the charge potential to be below 4.0 V is of crucial importance for realization of rechargeable Li-O_2 battery, and is currently a great challenge.

A Li-O_2 battery is based on the electrochemical reaction ($2Li + O_2 \leftrightarrow Li_2O_2$, $E^o = 2.96$ V). The discharge product Li_2O_2 is stored in the pores of cathode, that is, the discharge capacity is related to the porosity of cathode.[19,20] In order to improve the porous nature of cathode, carbon and carbon based materials were coated onto a carbon paper. Noticeably, the carbon paper may have somewhat activity towards oxygen reduction reaction (ORR). For the carbon-only cathodes, high charge potentials, typically 4.2 ~ 4.4 V, are ubiquitous.[14-20] Thereby, alternative porous supports other than carbon papers will be more suitable to evaluate the performance of Li-O_2 batteries and addition of an efficient catalyst towards oxygen evolution reaction (OER) in the charging process is necessary for reduction of charge overpotentials.

Varied catalysts have been attempted in non-aqueous Li-O_2 batteries, aiming at reduction of charge overpotentials. Nano-sized TiN supported on Vulcan XC-72 carbon black (VC) was tested in Li-O_2 batteries, and showed improved catalytic activity towards OER in charging processes.[21] But, it suffered the strong oxidative environment of the cathode and the supported TiN was partially converted to TiO_2 on cycling.[21] The composite of Co_3O_4, graphene and Ketjen black (KB) was demonstrated to present a large reduction of charge potential by 400 mV at 140 mA/g, compared with KB.[22] Other transition metal oxides and metal composites also contributed to the reduction of charge potential in non-aqueous Li-O_2 batteries.[17,18,22] In addition, noble metals have been actively studied for OER in aqueous solutions, while some of them have been studied as OER catalysts in non-aqueous Li-O_2 batteries.[18,23-25] Because the noble metals, like Pt and Pd,[26,27] possess strong catalytic activity to decompose electrolytes. Ru and RuO_2 have been reported to be good candidates as both the ORR and OER catalysts in non-aqueous Li-O_2 batteries.[23-25,28] Carbon spheres supported with both Co_3O_4 and RuO_2 nanoparticles were also attempted as a cathode in Li-O_2 batteries, in which the charge overpotentials and cyclability can be improved compared with the carbon-bare cathode.[29] Free-standing multi-walled carbon nanotube papers (MWCNTPs) have been demonstrated to deliver a huge specific capacity per mass, and the charge potential is typically approaching 4.4 V.[19] In this report, Ru nanoparticles were deposited onto a binder-free MWCNTP (denoted as Ru@MWCNTP) without a carbon paper support, as schematically shown in Scheme 1. The MWCNTs are interpenetrated together to form a porous network, which can provide facile transport of both electrons and oxygen. The supported Ru nanoparticles can function as both an ORR and OER catalyst. The resulted Li_2O_2 particles can be stored in the void spaces between MWCNTs and be efficiently decomposed by the MWCNTP supported Ru nanoparticles in a charging process. Simultaneously, the interpenetrated MWCNTs can reduce the effect of the volume changes upon the formation and decomposition of Li_2O_2 in the discharging and charging process on battery performance. The detailed performance of the Li-O_2 battery with Ru nanoparticles supported on MWCNTP as the cathode has been evaluated.



Scheme 1 Illustration of the discharging and charging processes of a Li-O_2 battery with Ru@MWCNTP as a cathode.

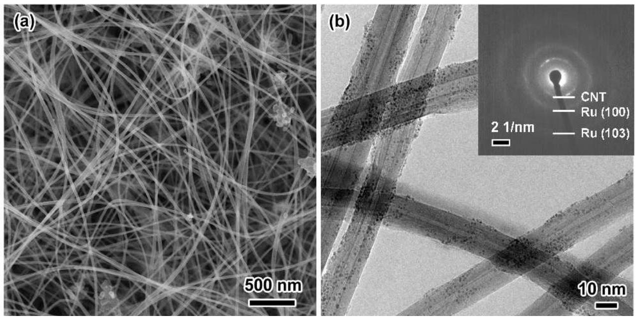


Fig. 1 SEM image (a) of MWCNTP and high-resolution TEM image of Ru@MWCNTP (b). The inset is a magnified TEM image of Ru nanoparticles on a MWCNT.

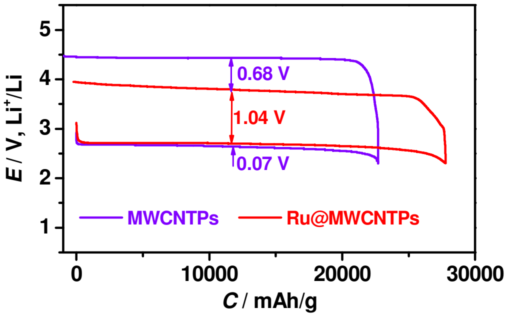


Fig. 2 Discharge/charge profiles of the Li-O_2 batteries with (a) MWCNTPs and (b) Ru@MWCNTPs at a current density of 500 mA/g in the 1st cycle. The employed electrolyte is a solution of LiTFSA and G3. The specific capacity and current are based on the total mass of MWCNTP and Ru@MWCNTP.

A typical SEM image of MWCNTP is shown in Fig. 1a, in which the MWCNTs are in the scale of micrometer and interpenetrated together. Large amounts of void spaces between MWCNTs can be obviously observed, which will be beneficial for the storage of Li_2O_2 particles in a discharging process. The small particles, iron encapsulated by carbon shown in Fig. 1a, were generated from the floated ferrocene vapor and functioned as the catalyst for the growth of MWCNTP in a tube furnace.[30,31] The size of MWCNTP can be easily adjusted by choosing different sized furnace tubes. The preparation flowchart and a typical photograph of a free-standing, centimetre-sized MWCNTP can be found in ESI†. The as-obtained MWCNTP was directly used without further treatment to support Ru nanoparticles that were formed in an ethylene glycol solution in advance.[32] The resulting Ru@MWCNTP is presented in the TEM image of Fig. 1b. The features of MWCNTs are clearly revealed: inner diameters of 5 to 10 nm and multiple interlayers of graphene, as shown in the inset of Fig. 1b. The Ru nanoparticles are ~ 2 nm and dispersed on the surface of MWCNTs (Fig. S2, ESI†). They can be confirmed by the energy dispersive X-ray spectroscopy (EDS, ESI†). The characteristic diffraction spots in the inset of Fig. 1b can be assigned to the facets of (100) and (103) of Ru, which can be further confirmed by the fast Fourier transform (FFT) in Fig. S3, ESI†. The loading of Ru in Ru@MWCNTP was estimated to 9.0 wt% via the thermogravimetric analysis (TGA, ESI†).

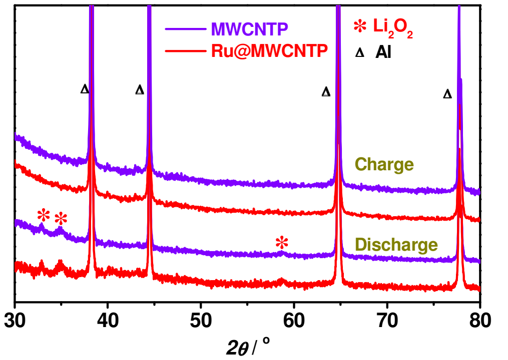


Fig. 3 XRD patterns of the discharged and charged cathodes of MWCNTP and Ru@MWCNTP.

The MWCNTPs with and without Ru nanoparticles were pressed onto Al meshes and worked as cathodes in Li-O_2 batteries with lithium bis(trifluoromethanesulfonyl)amide (LiTFSA) and triglyme (G3) with a molar ratio of 1 : 5 as the electrolyte. The discharge-charge curves of MWCNTP and Ru@MWCNTP at 500 mA/g are both presented in Fig. 2. A large specific capacity of 22600 mAh/g can be obtained in the MWCNTP cathode, which is smaller than 34600 mAh/g in our previous report 19. This may be due to the difference of the MWCNTPs prepared in different regions of the tube furnace. The charge potential of MWCNTP is high up to 4.42 V, similar to that in our previous report.[19] With the addition of Ru nanoparticles onto the MWCNTP, the charge potential is significantly reduced by 0.68 V in comparison with the bare MWCNTP, as shown in Fig. 2. The onset potential of Ru@MWCNTP is close to the theoretical value of 2.96 V, which is much lower than 3.29 V of MWCNTP. This suggests that Ru nanoparticles supported on the MWCNTP can efficiently catalyze the decomposition of the discharge product Li_2O_2. This observation also agrees with the previous reports involving Ru based catalysts.[24,25,28] In addition, Ru nanoparticles on MWCNTP with higher discharge potentials present more active catalytic activity towards ORR than the bare MWCNTP. The discharge and charge products in both MWCNTP and Ru@MWCNTP are examined by X-ray diffraction (XRD), and the corresponding results are shown in Fig. 3. In the discharging process, both MWCNTP and Ru@MWCNTP show the characteristic diffraction peaks of

Li_2O_2, as highlighted in Fig. 3, as well as the current collector Al mesh. This is consistent with the observation on Ru/ITO[25] and Ru supported on graphene[28]. It indicates that Li_2O_2 is the dominant crystalline product in the discharging process. When charged, the diffraction peaks of Li_2O_2 in both MWCNTP and Ru@MWCNTP disappear, meaning the reversible decomposition of Li_2O_2 in both cathodes. These results indicate the necessity of addition of Ru nanoparticles onto the MWCNTP which enable the superior ORR and OER catalytic activities of Ru@MWCNTP.

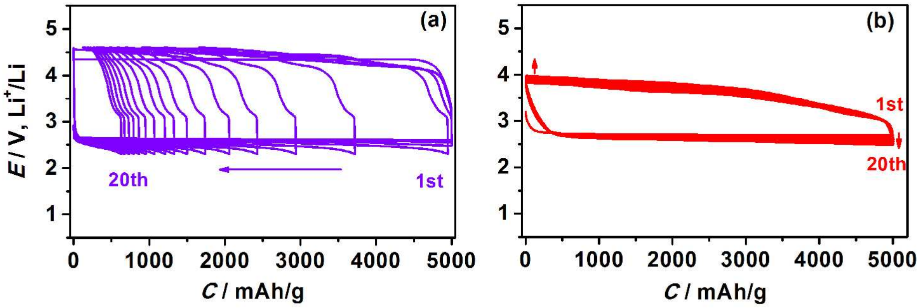


Fig. 4 Discharge/charge performance of the Li-O_2 batteries with MWCNTP (a) and Ru@MWCNTP (b) during 20 cycles with a cut-off capacity of 5000 mAh/g, at a current density of 500 mA/g.

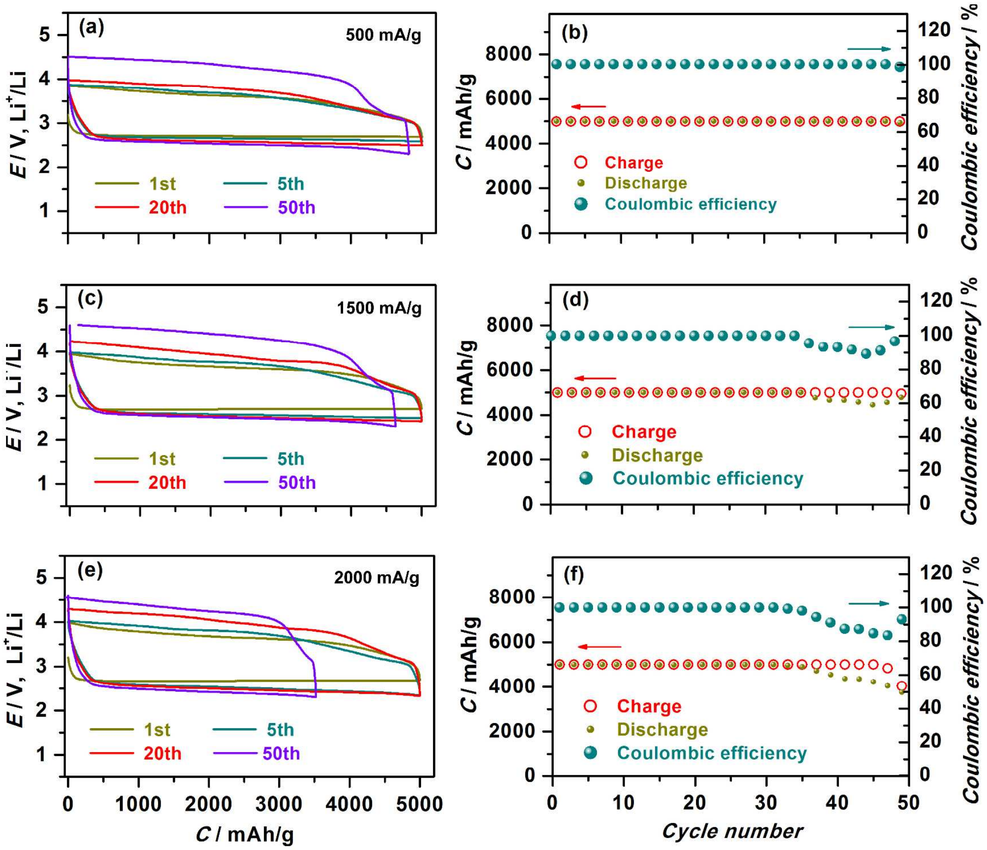


Fig. 5 Discharge/charge profiles of the Li-O_2 batteries with Ru@MWCNTP over 50 cycles with a cut-off capacity of 5000 mAh/g, at 500 mA/g (a), 1500 mA/g (c), and 2000 mA/g (e), and their corresponding cyclability and coulombic efficiency (b), (d), and (f).

With a cut-off capacity of 5000 mAh/g and at a current density of 500 mA/g, the Li-O_2 batteries with MWCNTP and Ru@MWCNTP are discharged and charged for 20 cycles and the corresponding profiles are depicted in Fig. 4. The charge potentials of MWCNTP are much higher than those of Ru@MWCNTP, consistent with Fig. 2. The discharge and charge capacity of MWCNTP is decaying quickly beyond the 2nd cycle. In a sharp contrast, there is a little variation in the discharge and charge profiles over the 20 cycles in the Li-O_2 battery with Ru@MWCNTP. In particular, the charge potentials of Ru@MWCNTP on cycling is below 4.0 V, which is crucially important for a rechargeable Li-O_2 battery. According to the previous reports with the electrolyte LiTFSA in G3 or other glyme based electrolytes, G3 is relatively robust towards oxygen radicals and can be attacked during long cycles. The resultant Li carbonate and Li alkylcarbonates can be partially decomposed in the following charging process.[15,19] The MWCNTs in the MWCNTP possess low catalytic activity towards either ORR or OER, as revealed in Fig. 2. Not all of the generated Li carbonate or Li alkylcarbonates in the MWCNTP can be decomposed in the charging processes, and the residues will be accumulated on cycling. This can induce large polarization, charging failure, and therefore capacity fading. While in the case of Ru@MWCNTP, Ru nanoparticles possess superior catalytic activity towards both ORR and OER, as demonstrated in Fig. 2. Most of the byproducts in the discharging process can be easily decomposed, which is evidenced by the much lower charging potentials in Ru@MWCNTP in Fig. 2 and Fig. 4b. This enables good cycling performance of Ru@MWCNTP over the 20 cycles in Fig. 4b. The reversible formation and decomposition of Li_2O_2 in the MWCNTP has been previously proved by XRD and SEM during cycles.[19]

As shown in Scheme 1 and Fig. 1, the Ru@MWCNTP is highly porous and composed of interpenetrated MWCNTs, which offers both facile electron and O_2 transport through the networks. Ru@MWCNTP with this particular configuration is further subjected to the evaluation of rate capability and cycling performance, as presented in Fig. 5. The discharge-charge cycles of the Li-O_2 batteries with Ru@MWCNTP at current density from 500, 1500 to 2000 mA/g with a cut-off capacity of 5000 mAh/g and their corresponding Coulombic efficiencies are obtained in Figs. 5(a, b), (c, d), and (e, f), respectively. The extended cycles of Fig. 4b is presented in Fig. 5a. Beyond the initial 20 cycles, the charge potential is gradually increased and reaches 4.5 V at the finish point of the 50th charge, as shown in Fig. 5a. The Coulombic efficiency during cycles is close to 100% at 500 mA/g. When the current density is increased to 1500 and 2000 mA/g, both of the Li-O_2 batteries can be discharged and charged for more than 30 cycles, as presented in Figs. (c, d) and (e, f), respectively. The charge potentials in both cases are increased quickly and reach the upper potential limit of 4.6 V. The Li-O_2 batteries can be charged for less than the cut-off capacity of 5000 mAh/g at the 50th charge. The discharge-charge cycles of Li-O_2 batteries with Ru@MWCNTP in Fig. 5 indicate good rate capability and cycling performance. This can be attributed to the superior ORR and OER catalytic activities of Ru@MWCNTP and the interpenetrated MWCNTs networks. In addition, the charge capacity is higher than the corresponding discharge capacity after 35 cycles with the charge potential higher than 4.27 V in Figs. 5c and e at 1500 and 2000 mA/g. It means that there may exist electrolyte decomposition at high potentials. These results may suggest: (i) electrolyte stability remains the bottleneck of long cycles, which is currently a great challenge; (ii) reducing the charge potential by adding a more active OER catalyst Ru onto MWCNTPs is necessary; and (iii) porous networks of cathodes enable large discharge-charge capacity and good rate capability.

Conclusions

Ru nanoparticles can be facilely deposited onto MWCNTPs and work as both an efficient ORR and OER catalyst. The resultant Ru@MWCNTP is demonstrated to efficiently reduce the charge potential below 4.0 V at 500 mA/g, in sharp contrast with the charge potential of 4.42 V on the bare MWCNTP. With a large cut-off capacity of 5000 mAh/g and at 500 mA/g, the Li-O_2 battery with Ru@MWCNTP can be discharged and charged for 20 cycles with stable discharge and charge potentials. This indicates the superior ORR and OER catalytic activity of Ru@MWCNTP. The Li-O_2 battery can also be cycled at high currents of 1500 and 2000 mA/g and presents good rate capability, which is attributed to the interpenetrated MWCNTs networks and Ru nanoparticles. Although 50 cycles of discharge and charge based on Ru@MWCNTP have been demonstrated here, long cycles will be dependent on the exploration of an ultimately stable electrolyte. Searching for a highly efficient OER catalyst for further reducing the charge potential will be equally important for the realization of rechargeable Li-O_2 batteries.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental process, flowchart of the preparation procedures of MWCNTP, and photograph, TEM/HRTEM images, and EDX and TGA of the Ru@MWCNTP. See DOI: 10.1039/b000000x/

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ARTICLE TYPE

Broader context

Energy storage and conversion devices with large specific energy density are attracting intense research. Li-O_2 battery is one of the most promising candidates. How to increase its low round-trip efficiency, namely, to reduce the high charge overpotentials, remains a great challenge. Designing different structured cathode materials and exploring efficient catalysts towards both oxygen reduction and oxygen evolution reactions have been demonstrated to improve Li-O_2 battery performance. This report presents a facile method to prepare a multi-walled carbon nanotube paper (MWCNTP) supported with Ru nanoparticles for Li-O_2 batteries. It can provide a large discharge/charge capacity, and significantly reduce the charge overpotentials and hence increase the round-trip efficiency.