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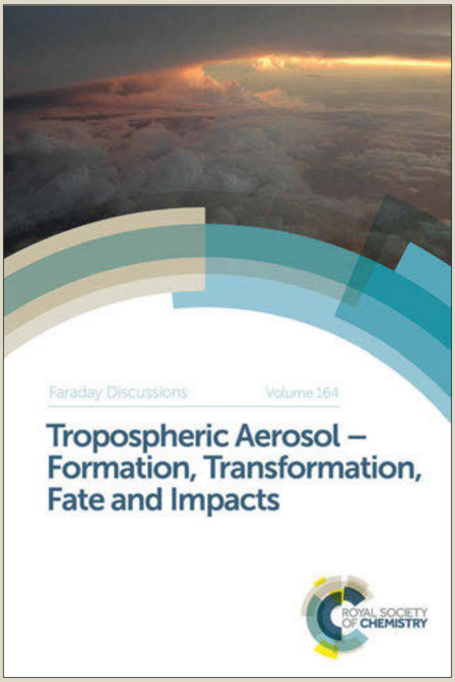

Faraday Discussions Volume 164

Tropospheric Aerosol – Formation, Transformation, Fate and Impacts

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COMMUNICATION

Reduced graphene oxide anchoring $CoFe_2O_4$ nanoparticles as effective catalyst for non-aqueous Lithium oxygen batteries

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$CoFe_2O_4$ nanoparticles were uniformly anchored on reduced graphene oxide by a facile solvothermal method. The obtained $CoFe_2O_4$/reduced graphene oxide ($CoFe_2O_4$/rGO) hybrid was employed as catalyst for Li-O_2 batteries. It could effectively lower the ORR and OER overpotentials of the batteries and deliver a large capacity of 12235 mAh/g_{rGO} (2116 mAh/g_{hybrid}). It also exhibited high cyclic stability.

Introduction

To meet the urgent energy demand of electric vehicles and large-scale energy storage, a new generation of lithium batteries, such as Li-air (O_2) battery, has become a popular research topic of scientists.[1, 2] As one of the metal-air batteries, Li-O_2 battery has an extremely high theoretical energy density of ~ 11500 Wh/Kg excluding the mass of O_2 that can be obtained from the atmosphere at discharging, which is higher than that of any battery and is equal to gasoline.[3]

In a typical Li-O_2 battery, the oxygen molecule is reduced to Li_2O_2 by combining with the lithium ions and electrons at the discharging process (oxygen reduction reaction, ORR) with a thermodynamic potential of 2.96 V, and recovered at the subsequent charging process (oxygen evolution reaction, OER).

However, large discharge and charge overpotentials exist due to the sluggish kinetics of the oxygen electrode, and thus resulting in low energy efficiency. In view of the poor rate capability and cyclic stability, current Li-O_2 batteries are still far from practical application.

Various electrocatalysts have been developed to improve the performance of the oxygen electrode, such as carbon materials, transition metal oxides and noble metals/oxides.[4-8] Graphene, an ideal two dimensional nanomaterial with unique physical and chemical properties, has been directly employed as catalyst for the oxygen electrode of Li-O_2 battery with significantly improved ORR performance than other carbon materials.[9, 10] It has also been used as the matrix for supporting transition metal oxides nanoparticles, such as MnO_2, Co_3O_4, to form composite materials with synergistic effects for both ORR and OER.[11-13] Covalent hybrids of spinel $MnCo_2O_4$ and $NiCo_2O_4$ own higher electrochemical activity as the ORR catalyst for Li-O_2 batteries than single oxide.[14, 15] $CoFe_2O_4$ has also been reported as catalyst for Li-O_2 battery by mechanically mixed with Super S and binder and showed moderate activity and cyclic stability, but also large discharge/charge overpotentail.[16] We therefore speculate that graphene supported $CoFe_2O_4$ would improve the performance of $CoFe_2O_4$ as the oxygen electrode catalyst.

Herein, we report a $CoFe_2O_4$/reduced graphene oxide ($CoFe_2O_4$/rGO) hybrid which was prepared from a facile one-pot solvothermal procedure. The hybrid exhibited superior catalytic property to pure rGO and its electrochemical performance as the oxygen electrode for Li-O_2 batteries was investigated in detail.

Experimental

Graphene oxide (GO) was prepared by the modified Hummers' method, while the $CoFe_2O_4$/rGO hybrid was synthesized by a solvothermal method. The detailed synthesis procedures are provided in the Supporting information.

The crystallographic information were investigated by powder X-ray diffraction (XRD, Philips X'pert Pro Super X-ray diffractometer using Cu Kα radiation with λ=1.5418 Å) at a 2θ range of 10-80°. The mass content of $CoFe_2O_4$ in the hybrid was determined by a Diamond TG/DTA analyzer (Perkin Elmer)

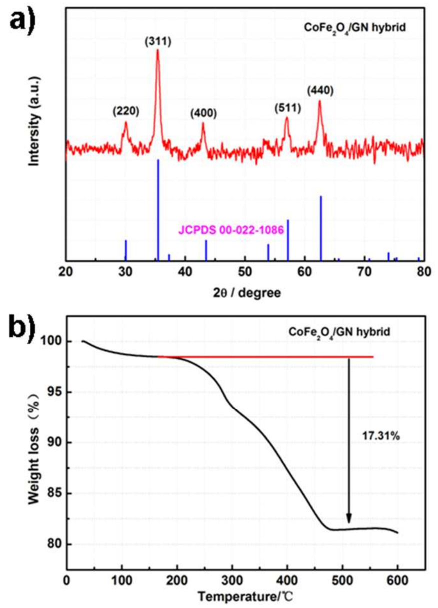

Fig. 1 a) The X-ray diffraction patterns of the $CoFe_2O_4$/rGO hybrid. b) The TG curve of the hybrid.

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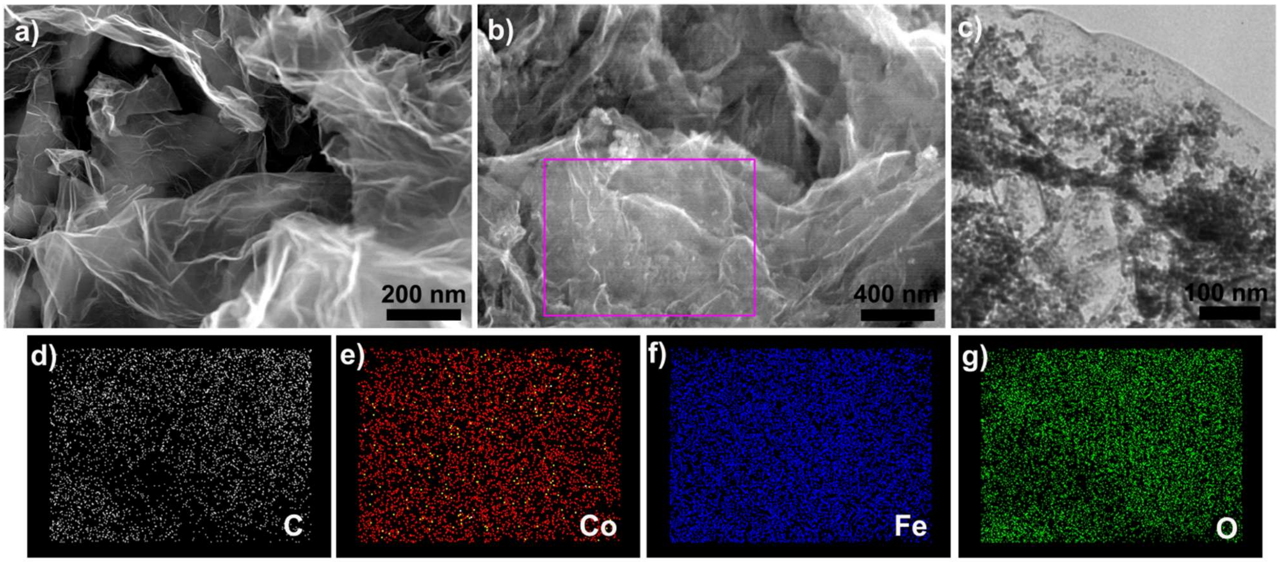

Fig. 2 a) An SEM image of the rGO. b) SEM and c) TEM images of the $CoFe_2O_4$/rGO hybrid. d)-g) Element distribution of C, Co, Fe and O of the selected area in Fig. 2b.

under a N_2/O_2 atmosphere at a heating rate of 5 □ min^{-1}. The detailed morphologies of the as prepared samples were characterized by field emission scanning electron microscopy (FESEM, HITACHI S-4800) and transmission electron microscopy (TEM, JEOL-1400).

The cathode was prepared by casting $CoFe_2O_4$/rGO hybrid and Kynar2801 (a copolymer based on PVDF) (by mass ratio of 9:1) onto a nickel foam current collector. A Swagelok type designed electrochemical cell composed of electrolyte (1M LiTFSI in TEGDME), a glass fiber membrane, a metallic lithium anode and the prepared cathode was used to test the electrochemical performance. The porous electrode was exposed to 1 atm O_2 atmosphere where the cell was tested in. All parts of the cell were dried in a 80 □ vacuum oven overnight before they were assembled into the Swagelok type cell in a Argon-filled glove box. Electrochemical performance of the cell was tested at room temperature using a Neware battery test system (Neware Co., Ltd, Shenzhen, China).

Results and discussion

X-ray diffraction (XRD) pattern of the as-prepared $CoFe_2O_4$/rGO hybrid is shown in **Fig. 1a**. All marked peaks can be indexed to spinel phase $CoFe_2O_4$ (JCPDS 00-022-1088) without any impurities. The calculated average particle size of the $CoFe_2O_4$ nanoparticle is about 13-15 nm based on the Scherrer equation. Note that the diffraction peak of the rGO cannot be observed in the pattern of the $CoFe_2O_4$/rGO hybrid, indicating the homogenous coating of $CoFe_2O_4$ nanoparticles on the rGO surface suppressing the stacking of graphene layers. The mass percentage of $CoFe_2O_4$ in the hybrid was measured by the TGA method as shown in **Fig. 1b**. The calculated mass content of $CoFe_2O_4$ is ~ 82.7%.

The morphology of the as prepared rGO is shown in Fig. 2a, which displays typical interconnected sheets with wrinkles on the surface. SEM and TEM images of the $CoFe_2O_4$/rGO hybrid are shown in **Fig. 2b and 2c**. The rGO matrix can maintain a dispersive status after the loading of $CoFe_2O_4$ nanoparticles. The TEM image in **Fig. 2c** confirms the well dispersion of $CoFe_2O_4$ nanoparticles on the rGO surface. Energy dispersive X-ray spectrometry (EDS) mapping in **Fig. 2d-g** and **Fig. S1** (Supporting information) provide additional evidence of $CoFe_2O_4$ on the rGO surface from the distribution of Co, Fe, O and C elements.

The N_2 adsorption-desorption isotherms and the pore-size distribution are shown in **Fig. S2**. The N_2 sorption isotherm has a shape of irreversible type IV, which is characteristic of mesoporous materials. The large degree of hysteresis between the adsorption and desorption isotherms is attributed to macropores form by graphene layers. The BJH pore-size-distribution shows that the major size of the pores falls into the range of 3-5 nm. The $CoFe_2O_4$/rGO hybrid has a BET specific surface area of 127 m^2/g and an average pore volume of 0.432 cm^3/g. The large surface area ensures sufficient reaction sites and the large pore volume is

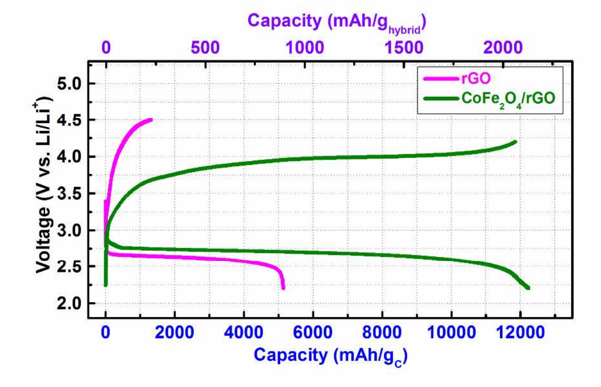

Fig. 3 A comparison of the voltage profiles of fully discharged Li-O_2 batteries with the $CoFe_2O_4$/rGO hybrid and pure rGO electrodes at the current density of 50 mA/g.

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favorable for the storage of discharging product.

The electrochemical performance of the $CoFe_2O_4$/rGO hybrid as the cathode of Li-O_2 batteries was evaluated by galvanostatic charge-discharge method. The voltage vs. capacity profile of a fully discharged/charged battery using $CoFe_2O_4$/rGO hybrid cathode is displayed in **Fig. 3**. Under a current density of 50 mA/g_{hybrid}, the battery delivered an extremely large discharge capacity of 12235 mAh/g based on the mass of rGO in the hybrid and a charge capacity of 11850 mAh/g within the voltage window of 2.2 V-4.2 V. The calculated coulombic efficiency is as high as 96.9%. The discharge and charge capacities based on the mass of the total hybrid (rGO+$CoFe_2O_4$) are 2116 and 2050 mAh/g, respectively, corresponding to the top label in **Fig. 3**. The discharge voltage platform is stable at around 2.7 V and the charge voltage platform is below 4.0 V. The energy efficiency was about 68% which is comparable with most of the reported transition metal oxides. For comparison, the performance of pure rGO was also tested under the same condition. Although it could deliver a discharge capacity of 5140 mAh/g, the discharge overpotential was about 0.1 V larger than the $CoFe_2O_4$/rGO hybrid. Worse still, the charge capacity was only 1322 mAh/g even under the cut-off voltage of 4.5 V, and no charge platform was observed due to the large charge overpotential. Therefore, a synergistic effect was achieved after the hybridization of rGO and $CoFe_2O_4$ nanoparticles, which improved both the ORR and OER processes of the Li-O_2 batteries.

The cyclic capability of the $CoFe_2O_4$ was also evaluated under a current density of 50 mA/g_{hybrid} with a cut-off capacity of 1000 mAh/g_C. The battery had no capacity decay over 30 cycles, as shown in **Fig. 4a.** The selected voltage profiles of different cycles are shown in **Fig. 4b**. The battery exhibited excellent cycle stability over 20 cycles without pronounced vibration in both the discharge and charge profiles. The discharge median voltage and terminal charge voltage are also recorded as shown in **Fig. 4c**. The initial discharge median voltage was 2.77 V and then slightly increased to 2.87 V in the subsequent five cycles. Although with slight voltage degradation afterward, it was still above 2.6 V after 30 cycles. During charging, the terminal voltage of the initial ten cycles was about 4.1 V, but it then dropped and stabilized at 4.0 V in the subsequent cycles.

The improved performance of the $CoFe_2O_4$/rGO hybrid can be attributed to the effective hybridization of nanoscaled $CoFe_2O_4$ particles and reduced graphene oxide. Firstly, rGO acts as the conductive matrix that is favorable for both electron-transport and electrolyte penetration into the electrode. The rGO matrix is highly dispersive and therefore benefits the oxygen diffusion. Secondly, $CoFe_2O_4$ particles are in-situ anchored on the rGO surface uniformly and act as effective catalyst for both ORR and OER. For one thing, the hybrid has a relatively high surface area and pore volume that can provide sufficient reaction sites and abundant space to store the discharging product Li_2O_2, promoting a large capacity delivery. For another, the $CoFe_2O_4$ nanoparticle with a diameter of ~15 nm enables fast reaction rate and short diffusion path lengths, resulting in fast kinetics of the oxygen electrode. Besides, it has been demonstrated that some carbon materials are not stable in the presence of Li_2O_2 and can be oxidized to Li_2CO_3 that are not easily to be decomposed during charging.[17] Also, defects on the carbon surface would also accelerate the decomposition of electrolyte, forming some by-products.[18] Some special electrode architecture in which carbon surface (defects) was coated by catalyst particles could efficiently prevent the formation of by-products.[8, 19] Therefore, although rGO used here is effective for ORR, but the large charge overpotential directly causes the battery degradation in the first charge process. While after the anchoring of $CoFe_2O_4$ on rGO surface, the ORR process was improved with lower discharging overpotential and large capacity due to the synergistic effect of rGO and $CoFe_2O_4$. More importantly, the OER overpotential was significantly reduced, which can not only be ascribed to the highly catalytic activity of $CoFe_2O_4$, but also the efficient prevention of the contact of rGO with Li_2O_2 by the $CoFe_2O_4$ particles.

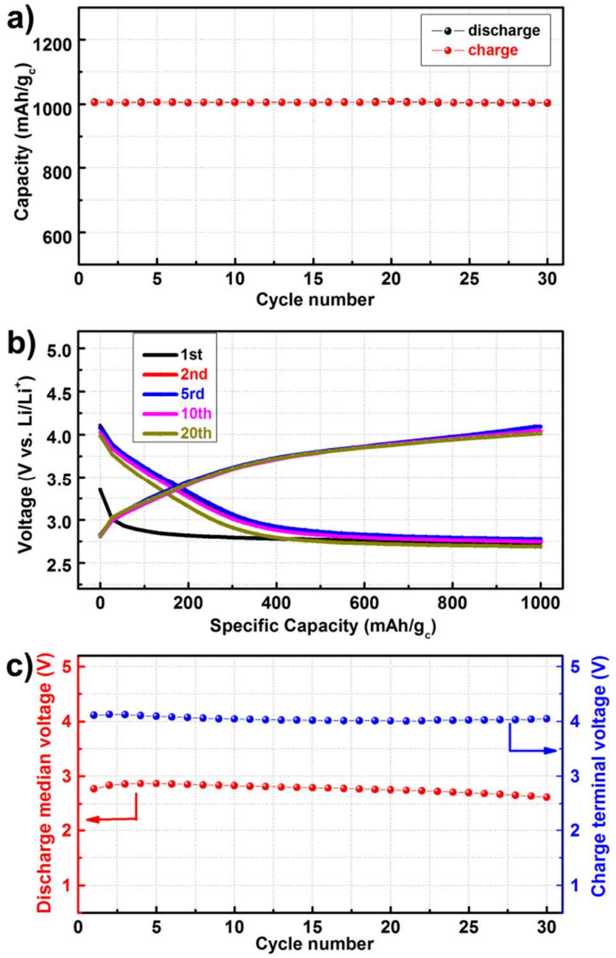

Fig. 4 a) Cycling stability of the Li-O_2 battery at a current density of 50 mA/g_{hybrid}. b) Discharging and charging profiles of the selected cycles. c) The variation of discharge median voltage and charge terminal voltage with the cycle number.

Conclusions

In summary, a $CoFe_2O_4$/rGO hybrid was prepared through a facile solvothermal reaction. When employed as the oxygen cathode of Li-O_2 batteries, the $CoFe_2O_4$/rGO hybrid demonstrated bifunctional catalytic activity for both ORR and OER. It showed extremely higher specific capacity and energy efficiency than pure rGO. The improved performance can be attributed to the

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synergistic effect of the hybrid. The rGO acted as the conductive matrix that is favorable for both electron-transport and electrolyte penetration, while the anchored $CoFe_2O_4$ nanoparticles exhibited the catalytic role. Although some improvement has been achieved, the OER overpotential is still too large. So further study will be focused on the optimization of this type of catalyst.

Notes and references

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