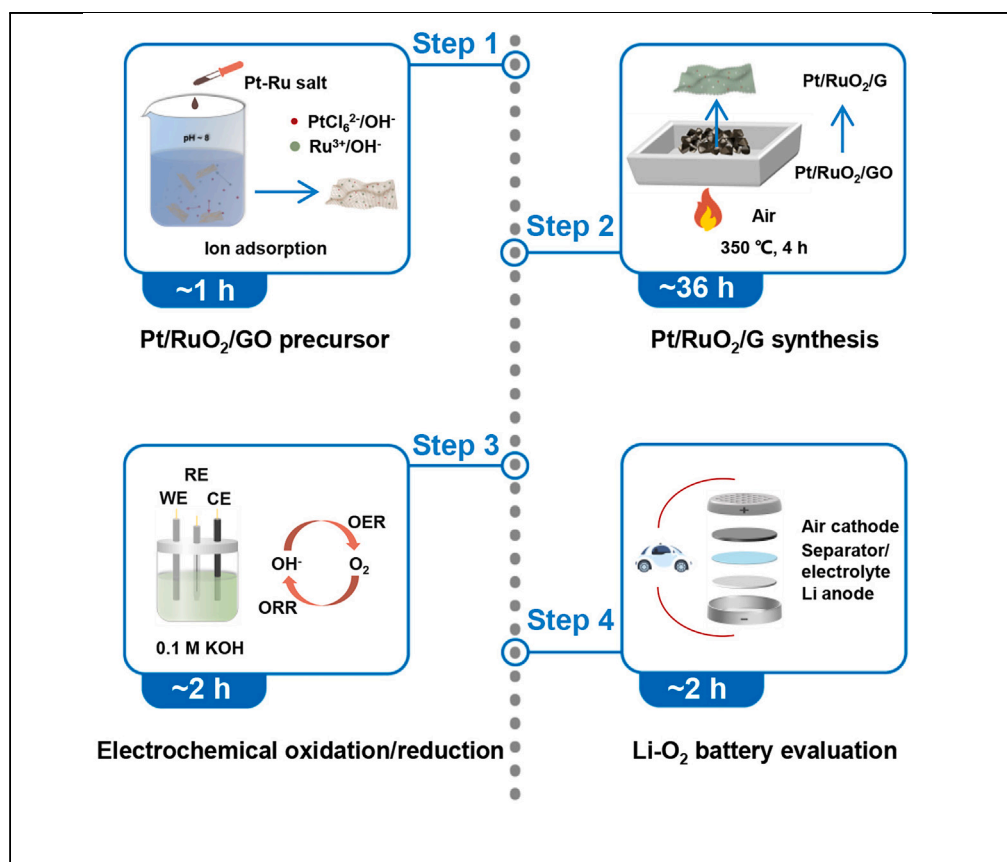


Protocol

Protocol for fabrication of Pt/RuO₂/graphene bifunctional oxygen catalyst in Li-O₂ batteries



Yuejiao Li, Lisha Wu,
Yajun Ding, Zhong-
Shuai Wu

wuzs@dicp.ac.cn

Highlights

Detailed preparation of Pt/RuO₂/graphene bifunctional oxygen electrocatalyst

Oxygen electrocatalyst measurements of Pt/RuO₂/graphene in 0.1 M KOH

Nonaqueous Li-O₂ batteries evaluation of Pt/RuO₂/graphene cathode

The commercial mass production of bifunctional oxygen catalysts with high activity and stability is critical for constructing high-performance lithium-oxygen (Li-O₂) batteries, but remains challenging. Herein, we describe a protocol for the scalable fabrication of a 2D bifunctional electrocatalyst of Pt/RuO₂/graphene by spatial confinement strategy and elaborately evaluate its oxygen reduction/evolution reactions for advanced Li-O₂ batteries. We then detail the synthesis steps for preparing materials followed by assembly and evaluation of the three-electrode systems and coin-type Li-O₂ batteries.

Publisher's note: Undertaking any experimental protocol requires adherence to local institutional guidelines for laboratory safety and ethics.

Li et al., STAR Protocols 4,
102746
December 15, 2023 © 2023
The Authors.
<https://doi.org/10.1016/j.xpro.2023.102746>



Protocol

Protocol for fabrication of Pt/RuO₂/graphene bifunctional oxygen catalyst in Li-O₂ batteriesYuejiao Li,¹ Lisha Wu,¹ Yajun Ding,¹ and Zhong-Shuai Wu^{1,2,3,*}¹State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China²Technical contact³Lead contact*Correspondence: wuzs@dicp.ac.cn
<https://doi.org/10.1016/j.xpro.2023.102746>

SUMMARY

The commercial mass production of bifunctional oxygen catalysts with high activity and stability is critical for constructing high-performance lithium-oxygen (Li-O₂) batteries, but remains challenging. Herein, we describe a protocol for the scalable fabrication of a 2D bifunctional electrocatalyst of Pt/RuO₂/graphene by spatial confinement strategy and elaborately evaluate its oxygen reduction/evolution reactions for advanced Li-O₂ batteries. We then detail the synthesis steps for preparing materials followed by assembly and evaluation of the three-electrode systems and coin-type Li-O₂ batteries.

For complete details on the use and execution of this protocol, please refer to Li et al. (2023).¹

BEFORE YOU BEGIN

Li-O₂ batteries possess the key characteristics of sustainability, green friendliness and ultra-high theoretical energy density, which can satisfy the next-generation development demand of new energy vehicles.^{2,3} To this goal, the exploration of bifunctional electrocatalysts with high efficiency towards oxygen reduction reaction and oxygen evolution reaction (ORR/OER) has attracted much attention to solve the bottleneck issues in Li-O₂ batteries, such as unsatisfactory overpotential and limited cyclability.^{4,5} Currently, precious metals catalysts show remarkable advantages in various electrochemical catalytic reactions. However, their single catalytically active site, poor stability and high cost seriously hinder the further industrial application.^{6,7} Therefore, the design of bifunctional precious metal-based catalysts with high activity and stability is crucial to promote its commercialization of Li-O₂ batteries. In this protocol, we report the synthesis of a remarkably active and durable bifunctional electrocatalyst by synergistically coupling the ORR catalyst Pt with the OER catalyst RuO₂ on conductive graphene (denoted as Pt/RuO₂/G). Subsequently, the Pt/RuO₂/G electrocatalysts are assembled in the three-electrode systems and the coin-type Li-O₂ batteries to evaluate their electrochemical behavior. This general protocol can be applied to integrate the composite catalysts for bifunctional active sites.

KEY RESOURCES TABLE

REAGENT or RESOURCE	SOURCE	IDENTIFIER
Chemicals, peptides, and recombinant proteins		
Chloroplatinic acid (H ₂ PtCl ₆ ·6H ₂ O), AR	Aladdin	CAS: 16941-12-1
Ruthenium chloride (RuCl ₃ ·3H ₂ O), 98%	Macklin	CAS: 10049-08-8

(Continued on next page)



Continued

REAGENT or RESOURCE	SOURCE	IDENTIFIER
Sodium hydroxide (NaOH), AR	Sinopharm	CAS: 1310-73-2
Platinum on carbon (Pt/C), Pt 20%	Macklin	CAS: 7440-06-4
Ruthenium (IV) oxide (RuO ₂), 99.9%	Aladdin	CAS: 12036-10-1
Potassium hydroxide (KOH), AR	Sinopharm	CAS: 1310-58-3
Hydrochloric acid (HCl, 36%–38%)	Sinopharm	CAS: 7647-01-0
N-methyl pyrrolidone (NMP), AR	Kermel	CAS: 872-50-4
Polyvinylidene fluoride (PVDF), AR	DuoDuo	CAS: 24937-79-9
Nafion, AR	DuPont	D520
Other		
Glassy carbon electrode for ORR (round disk electrode [RDE, ϕ 5]; rotating ring-disk electrode [RRDE] with a Pt ring of 6 mm inner diameter and 8.5 mm outer diameter)	-	http://www.pineinst.com/
Glassy carbon electrode for OER (ϕ 3)	-	http://www.gaossunion.com/
Carbon rob electrode	-	http://www.gaossunion.com/
Ag/AgCl electrode	-	http://www.gaossunion.com/
Carbon paper	-	http://www.hesen.cn/
Li foil	-	http://www.yirikj2012.com/
1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in tetraethylene glycol dimethyl ether (TEGDME)	DuoDuo	https://www.dodochem.com/
Separator	Whatman	Cat No. 1820-125
Electrochemical workstation (ORR testing, software: AfterMath)	Phychemi Co., Ltd.	AFMSRCE
Electrochemical workstation (OER testing, software: Chi760e)	Shanghai Chenhua Co., Ltd.	CHI 760E
LAND testing station (Li-O ₂ batteries testing, software: Land)	Wuhan LAND Electronic Co., Ltd.	CT3001A

MATERIALS AND EQUIPMENT

Pt/RuO₂/graphene oxide (GO) precursor solution

Reagent	Final concentration	Amount
GO	~0.95 mg mL ⁻¹	20 mL
H ₂ PtCl ₆	~0.38 mg mL ⁻¹	0.4 mL
RuCl ₃	~0.57 mg mL ⁻¹	0.6 mL
NaOH	~0.24 mg mL ⁻¹	0.1 mL
Deionized H ₂ O	-	21.1 mL
Total	-	21.1 mL

Note: The Pt/RuO₂/GO precursor solution should be freshly made and stored at 25°C before use. Its final pH should be ~8.

STEP-BY-STEP METHOD DETAILS

Synthesis of Pt/RuO₂/graphene oxide precursor

⌚ **Timing:** ~0.5 h aqueous solution preparation, ~0.5 h stirring, ~12 h freeze drying

The Pt/RuO₂/graphene oxide (Pt/RuO₂/GO) precursor was synthesized by using an ion adsorption strategy to uniformly adsorb ruthenium cations (Ru³⁺) and subsequent chloroplatinic acid anions (PtCl₆²⁻) on the surface of single-layer GO nanosheets followed by freeze drying, as shown in [Figure 1](#). (If necessary, the amount of reactants can be expanded to obtain more products.)

1. Prepare graphene oxide (GO) solution by hummers' method.

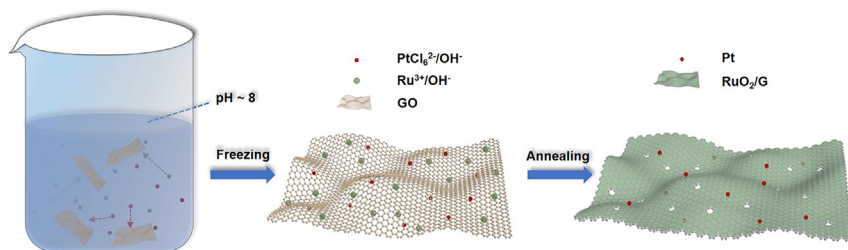


Figure 1. Scheme of the fabrication procedure of 2D Pt/RuO₂/G electrocatalyst

Figure reprinted with permission from Li et al., 2023.

2. Dilute GO solution with deionized water to a concentration of 1 mg mL⁻¹.
3. Prepare 0.6 mL of RuCl₃ aqueous solution and 0.4 mL of H₂PtCl₆ aqueous solution at a concentration of 20 mg mL⁻¹, and 1 mL of NaOH aqueous solution at a concentration of 50 mg mL⁻¹.
4. Mix the RuCl₃ solution and H₂PtCl₆ solution with stirring for ~5 min, and then add drop by drop (~1 drop min⁻¹) the above solution (1 mL) into 20 mL GO solution under stirring at a speed of ~400 rpm for 0.5 h.
5. Add 0.1 mL NaOH aqueous solution into the mixed solution with continuous stirring at a speed of ~400 rpm.
6. Freeze-dry of the above mixture in liquid nitrogen for 12 h.

⚠ **CRITICAL:** When using liquid nitrogen, the operators should wear protective gloves to prevent frostbite.

Note: The drop acceleration of Pt-Ru mixed solution should not be too fast to avoid solution coagulation.

Synthesis of Pt/RuO₂/G electrocatalyst

⌚ **Timing:** ~6 h annealing, ~ 2 h washing, ~2 h drying

The 2D Pt/RuO₂/G nanosheets were obtained by annealing the freeze-dried product, followed by washing and drying (Figure 2).

7. The whole freeze-dried products were maintained at 350°C for 4 h in the muffle furnace.
8. Soak the Pt/RuO₂/G in 5 mL of 1 M dilute hydrochloric acid to remove excess NaOH, and then filter the mixed solution with deionized water several times (more than 3 times) to remove Na⁺ and Cl⁻ ions.

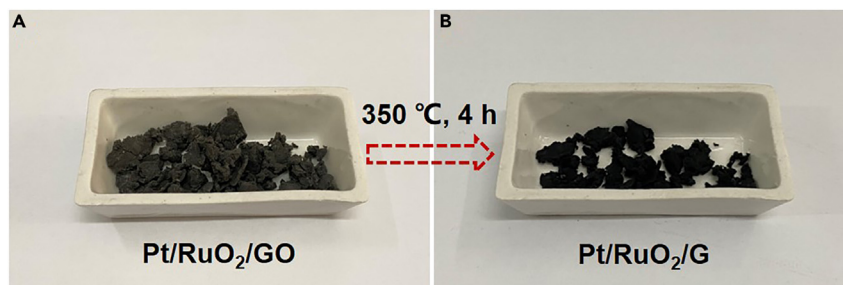


Figure 2. Preparation of Pt/RuO₂/G by calcination of Pt/RuO₂/GO at 350 °C for 4 h

(A) The Pt/RuO₂/GO precursor obtained after freeze-drying.

(B) The Pt/RuO₂/G product obtained after annealing.

9. Dry the Pt/RuO₂/G in a vacuum oven for 2 h at 80°C.

△ **CRITICAL:** Hydrochloric acid is corrosive and volatile; the operators should wear protective gears and handle it in a fume hood when diluting the hydrochloric acid.

Preparation of the working electrode in three-electrode systems

⌚ **Timing:** ~1 h electrode preparation, ~2 h electrochemical measurement

Homogeneous catalyst inks were prepared and coated on glassy carbon electrodes, followed by assembly of standard three-electrode systems and evaluation of bifunctional catalytic activity (Figure 3).

10. Add 2 mg of Pt/RuO₂/G electrocatalyst and 20 μL of 5 wt % Nafion solution in a mixed solution of 1 mL ethanol and water with a volume ratio of 1:1, followed by sonication for at least 30 min.
11. Drop 5 μL and 15 μL catalyst ink by the pipette onto the surface of glassy carbon (ϕ5 for ORR and ϕ3 for OER) electrode, respectively.
12. Dry the electrodes under an infrared lamp for about ~30 min.
13. Construct the three-electrode measurement system with the as-prepared working electrode, the counter electrode of carbon rob and the reference electrode of Ag/AgCl in 0.1 M KOH electrolyte.
14. Activate the catalysts to a stable state via cyclic voltammetry (CV) scanning with a sweep rate of 50 mV s⁻¹ (ORR: 0.1 to -0.9 V, OER: 0-0.7 V, vs. Ag/AgCl) in the N₂ and O₂-saturated electrolyte.
 - a. Conduct the linear sweep voltammetry (LSV) with a sweep rate of 5 mV s⁻¹ (ORR: different rotation rate from 400 to 2025 rpm; OER: potentials compensation by *i*R 90%).
 - b. Collect the electrochemical impedance spectroscopy spectra at 0.5 V (vs. Ag/AgCl) in the frequency range from 0.01 Hz to 100 kHz and amplitude of 5 mV.

△ **CRITICAL:** When configuring the electrolyte and assembling the three-electrode system, the operator should wear protective gloves to avoid irritation of the skin by KOH.

Note: Ensure that the KCl solution filled in the reference electrode is saturated.

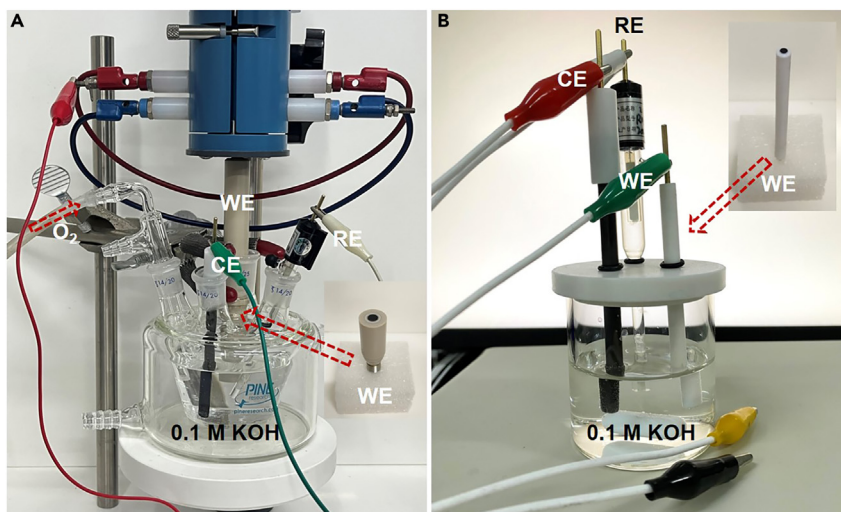


Figure 3. Experimental set-up for three-electrode systems

(A and B) Typical optical photographs of the electrochemical cell for (A) ORR and (B) OER measurements.

Preparation of the air-cathode for Li-O₂ batteries

Ⓞ Timing: ~12 h electrode preparation, ~1 h assembling, over 1,000 h stability measurement

The mixed slurry was prepared and coated on carbon paper air-cathode, followed by assembly of coin-type Li-O₂ batteries and evaluation of battery performance (Figure 4).

15. Cut the carbon paper into the discs with a diameter of 16 mm as the current collectors, and mark the initial mass.
16. Disperse ~2.7 mg of catalysts and ~0.3 mg of PVDF in 1~2 drops of NMP and then grind it into a homogeneous slurry.
17. Coat the slurry on the surface of the current collectors with a brush and dry at 100°C in vacuum oven for 10 h.
18. Record the mass of the air-cathode after drying to calculate the loading.
19. Construct the coin-type Li-O₂ batteries in a glove box filled with argon with the as-prepared air-cathode, the separator containing 70 μL of 1 M LiTFSI/TEGDME electrolyte, Li anode with a diameter of 16 mm.
20. Transfer the batteries to the box filled with oxygen for Li-O₂ batteries testing.
 - a. Conduct the CV measurements (1.5–4.5 V, 0.1 mV s⁻¹) and galvanostatic discharge-charge (GCD) profiles (current density: 200 mA g⁻¹, capacity limitation: 1000 mAh g⁻¹).
 - b. Collect the specific capacity plots between 2–4.5 V (current density of 100, 200, and 500 mA g⁻¹).

Note: Make sure that all components involved in assembling batteries are kept away from H₂O.

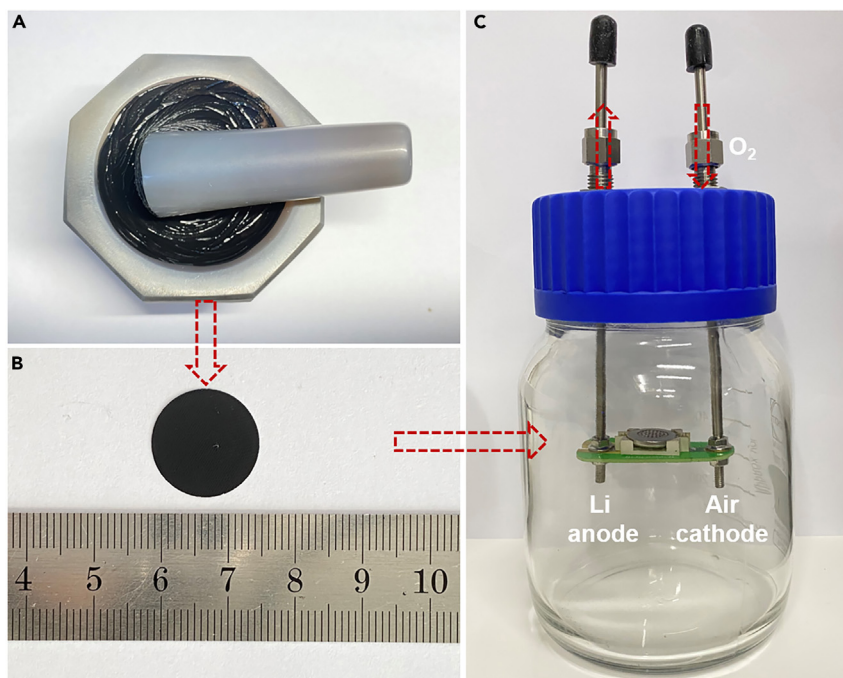


Figure 4. Construction of the coin-type Li-O₂ batteries

(A) Optical image of the slurry with Pt/RuO₂/G catalyst after grinding.

(B) Optical image of the air-cathode coated with the slurry.

(C) A typical optical photograph of the experimental set-up for Li-O₂ batteries measurements.

EXPECTED OUTCOMES

This protocol provides a straightforward and reliable strategy for designing bifunctional electrocatalysts in Li-O₂ batteries. The as-prepared Pt/RuO₂/G nanosheets present the ultrathin thickness, small size of RuO₂ nanoparticles and uniformly dispersed sub-nanometer Pt under the effect of spatial confinement (Figure 5). As a result, Pt/RuO₂/G electrocatalyst exhibits excellent performance in oxygen catalysis with a low OER/ORR voltage gap of 0.633 V, and offers a prolonged cycling stability of over 2200 h for Li-O₂ batteries (Figure 6). This work provides a reliable practical approach for the realization of highly active and mass-produced bifunctional catalytic material and air-cathode electrocatalysts for Li-O₂ batteries which are expected to be commercialized.

LIMITATIONS

The main limitation of this protocol is that the constructed Li-O₂ battery needs to be measured in a pure oxygen atmosphere, which hinders the real commercialization. Therefore, the development of a type of oxygen-permeable exchange membrane or the design of solid-state electrolyte is critical for realizing the actual application of Li-air batteries.

TROUBLESHOOTING

Problem 1

The mixed solution may coagulate after adding Pt-Ru salt (step 4).

Potential solution

Dilute the GO solution and configure the Pt-Ru mixed solution with the deionized water at low temperature about 4°C.

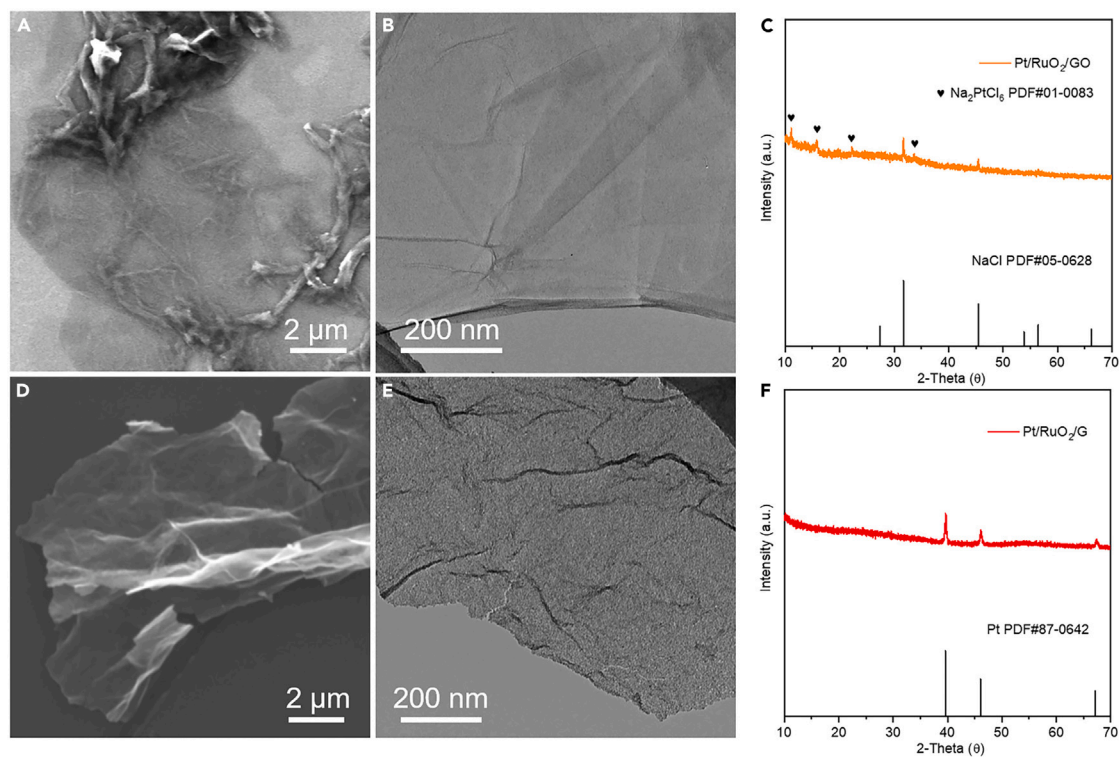


Figure 5. Characterization of (A–C) Pt/RuO₂/GO precursor and (D–F) Pt/RuO₂/G

Figure reprinted with permission from Li et al., 2023.

(A and D) Scanning electron microscopy (SEM) images.

(B and E) Transmission electron microscopy (TEM) images. (C and F) X-ray diffraction (XRD) patterns.

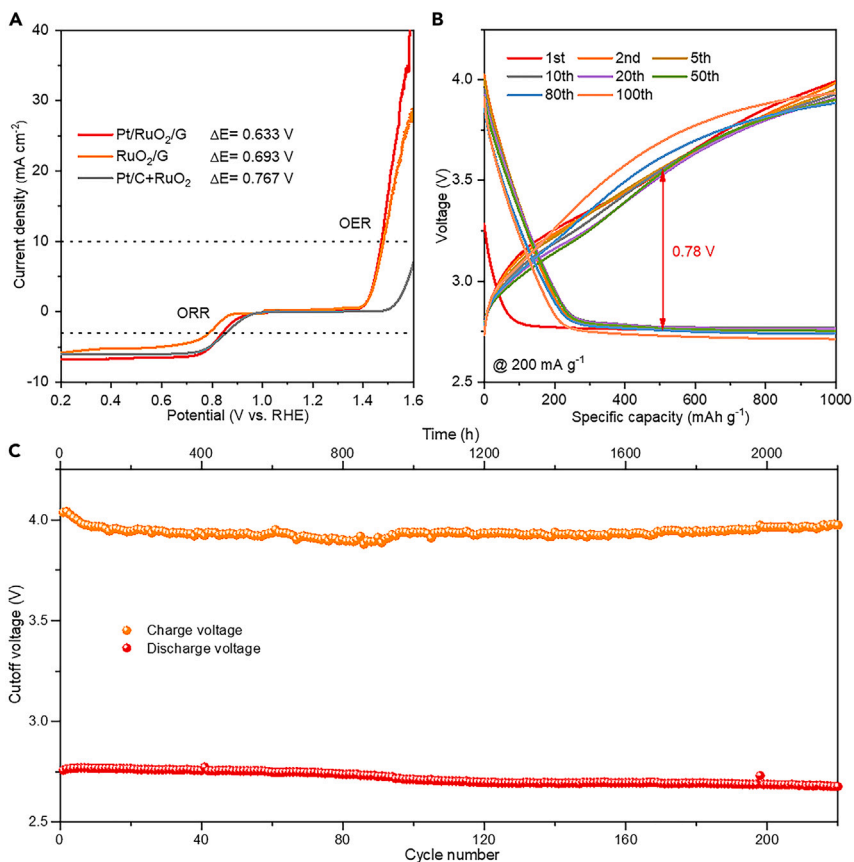


Figure 6. Electrochemical performance of Pt/RuO₂/G bifunctional electrocatalyst for OER/ORR and Li-O₂ batteries

Figure reprinted with permission from Li et al., 2023.

(A) OER/ORR chronoamperometric curves.

(B and C) GCD profiles of Li-O₂ batteries.

Problem 2

The heterogeneous dispersion of catalyst results in the inability to form a uniform film on the surface of glassy carbon electrode (steps 11 and 12).

Potential solution

Grind the catalyst prior to ink preparation, and additionally, preferentially disperses the material by means of ultrasonic cell crusher.

Problem 3

Unsmoothness of LSV curve due to massive oxygen generation during OER process (step 14).

Potential solution

Add the magnetons to the cell and adjust the appropriate speed to ensure the rapid diffusion of oxygen produced during OER.

Problem 4

Air humidity problems cause water absorption during grinding slurry (steps 16 and 17).

Potential solution

The slurry is prepared on a heating table and the humidity is kept below 30%. Moreover, the dried air-cathode is quickly transferred to the Ar glove box for storage to avoid excessive exposure to the air.

Problem 5

The poor gas tightness of the test atmosphere causes contaminants such as CO₂ and H₂O to affect the stability of the Li-O₂ batteries (step 20).

Potential solution

Use a box with good airtightness and add desiccant. In addition, the battery for testing long-term stability can be constructed in an oxygen-atmosphere glove box.

RESOURCE AVAILABILITY

Lead contact

Further information and requests for resources should be directed to and will be fulfilled by the lead contact, Zhong-Shuai Wu (wuzs@dicp.ac.cn).

Materials availability

This protocol did not generate new unique reagents.

Data and code availability

Data and code generated during this study are available from the lead contact upon request.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (grant nos. 22209181 and 22125903), Dalian Innovation Support Plan for High-Level Talents (2019RT09), the Dalian National Laboratory For Clean Energy (DNL), CAS, the DNL Cooperation Fund, CAS (DNL202016 and DNL202019), and DICP (DICP I2020032 and DICP I202222).

AUTHOR CONTRIBUTIONS

Z.-S.W. conceived the experiments and supervised this project. Y.L., L.W., and Y.D. performed the experiments and the analysis. Y.L. and Z.-S.W. wrote the manuscript. All the authors discussed the results and commented on the manuscript.

DECLARATION OF INTERESTS

The authors have a Chinese patent related to this work.

REFERENCES

- Li, Y., Li, Y., Ding, Y., Ma, J., Das, P., Zhang, B., Wu, Z.-S., and Bao, X. (2023). Spatially confined sub-nanometer Pt in RuO₂ nanosheet as robust bifunctional oxygen electrocatalyst for stabilizing Li-O₂ batteries. *Chem Catal.* 3, 100658.
- Kwak, W.J., Rosy Sharon, D., Sharon, D., Xia, C., Kim, H., Johnson, L.R., Bruce, P.G., Nazar, L.F., Sun, Y.K., Frimer, A.A., et al. (2020). Lithium-oxygen batteries and related systems: potential, status, and future. *Chem. Rev.* 120, 6626–6683.
- Zhang, P., Zhao, Y., and Zhang, X. (2018). Functional and stability orientation synthesis of materials and structures in aprotic Li-O₂ batteries. *Chem. Soc. Rev.* 47, 2921–3004.
- Bruce, P.G., Freunberger, S.A., Hardwick, L.J., and Tarascon, J.M. (2011). Li-O₂ and Li-S batteries with high energy storage. *Nat. Mater.* 11, 19–29.
- Wang, H., Wang, X., Li, M., Zheng, L., Guan, D., Huang, X., Xu, J., and Yu, J. (2020). Porous materials applied in nonaqueous Li-O₂ batteries: status and perspectives. *Adv. Mater.* 32, e2002559.
- Zhao, Z., Chen, C., Liu, Z., Huang, J., Wu, M., Liu, H., Li, Y., and Huang, Y. (2019). Pt-based nanocrystal for electrocatalytic oxygen reduction. *Adv. Mater.* 31, e1808115.
- Shi, Q., Zhu, C., Du, D., and Lin, Y. (2019). Robust noble metal-based electrocatalysts for oxygen evolution reaction. *Chem. Soc. Rev.* 48, 3181–3192.