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A dismutase-biomimetic bifunctional mobile catalyst for anti-aging lithium–oxygen batteries

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HIGHLIGHTS

- The superoxide dismutase mimics (SODm) to improve the ORR and OER in Li–O₂ battery.
- The discharge reaction via solution pathway is facilitated by the SODm.
- The energy barrier of lithium superoxide disproportionation is lowered by the SODm.
- The catalyzed disproportionation reaction by the SODm reduce the superoxide lifetime.

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ABSTRACT

Aprotic lithium-oxygen batteries (LOBs) have been considered as one of the high-energy-density alternatives to replace currently available lithium ion batteries. Highly reactive superoxide as the discharge intermediate of LOBs triggers side reactions to deteriorate LOB performances. Also, high overpotential is required to oxidize the discharge product Li₂O₂ during charge due to the non-conductive nature of Li₂O₂. Herein, we present 4-carboxy-(2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO-COOH) as a superoxide dismutase mimetic bifunctional mobile catalyst soluble in electrolytes for improving LOB performances. The role of TEMPO-COOH is two-fold: (1) the chemo-catalyst to catalyze superoxide disproportionation reaction for suppressing the superoxide-triggered side reactions during discharge; and (2) the redox mediator to oxidize Li₂O₂ in a kinetically effective way for reducing the overpotential during charge. The use of the mobile catalyst in LOB cells resulted in the 4-fold increase in cycle life from 50 cycles to 200 cycles as well as the 4-fold increase in the discharge capacity, significantly reducing the overpotential during charge.

1. Introduction

Rechargeable aprotic lithium-oxygen batteries (LOBs) have attracted significant interests because of their energy density much higher than that of today's lithium ion batteries [1–9]. LOBs generate electricity at < 2.96 V by reducing oxygen to lithium peroxide ($O_2 + 2Li^+ + 2e^- \rightarrow Li_2O_2$) by using electrons obtained from lithium metal ($Li \rightarrow Li^+ + e^-$). A typical LOB consists of a lithium metal anode and a porous air cathode with an aprotic electrolyte. The major challenges limiting cycle life of LOBs and increasing overpotentials are (1) chemical instability of electrolyte molecules and cathode materials during discharge and charge, (2) isolation of cathode surface from oxygen species in electrolyte by

discharge products and (3) incomplete splitting of lithium peroxide back to oxygen and lithium ion during charge [1,10].

During discharge, O₂ is reduced to Li₂O₂ on the cathode via two different routes depending on the surrounding conditions such as Li₂O₂ solubility of the electrolyte or current density [11–15]. In the beginning of discharge, O₂ is reduced to superoxide radical (O₂^{•−}) and combined with Li⁺ to be LiO₂. The insoluble LiO₂ on the surface of air cathode undergoes further electrochemical conversion with an additional e[−] from the cathode and Li⁺ to be film-like Li₂O₂ (surface mechanism). Alternatively, the LiO₂ could be solvated by electrolyte solvent and disproportionated to be toroidal Li₂O₂ particles on the air cathode (solution mechanism). It should be noticed that the solution mechanism for

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