
Supporting Information

Intensive Study on the Catalytical Behavior of N-Methylphenothiazine as a Soluble Mediator to Oxidize the Li_2O_2 Cathode of the Li- O_2 Battery

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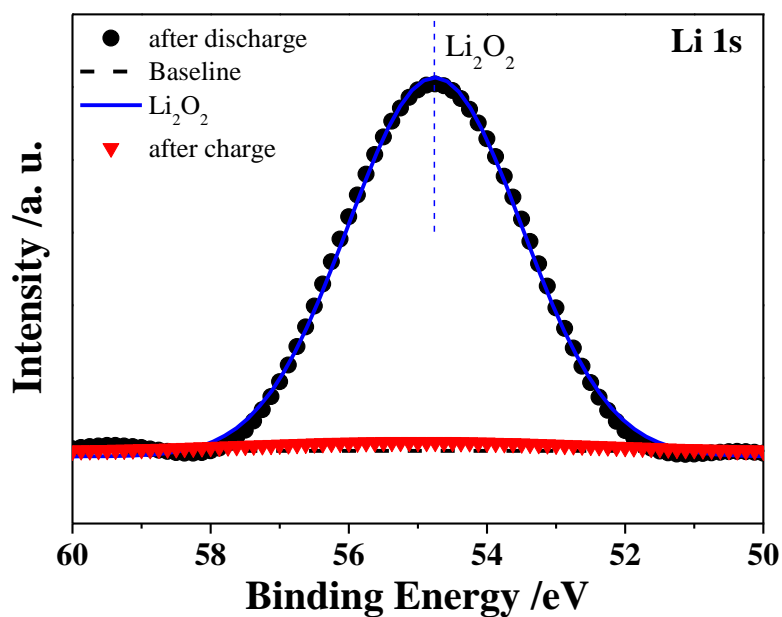


Figure S1. Li 1s XPS spectra of the Super P electrodes after discharge and recharge in a 0.1 M MPT/1.0 M LiCF₃SO₃/TEGDME electrolyte. The peak of Li 1s (54.7 eV) can be assigned to Li₂O₂, and no Li₂CO₃ was detected. After recharge process, the peak of Li₂O₂ was disappeared. This results indicated the reversible formation/decomposition of Li₂O₂ occur at the oxygen cathode.

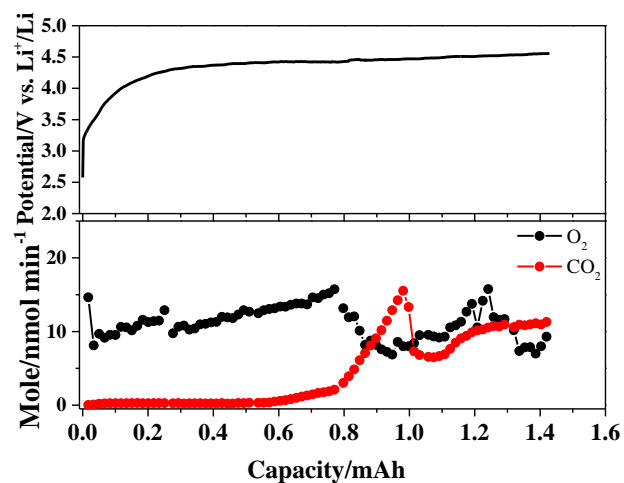


Figure S2. Gases evolution and corresponding galvanostatic charge profiles for a Li-O₂ cell with Super P cathode and without MPT mediator under the same testing condition with Figure 4. The peak in the CO₂ evolution in the 4.4-4.6 V suggests that solid carbonate deposits result both from reaction of Li₂O₂ with the C cathode and from decomposition of the electrolyte.

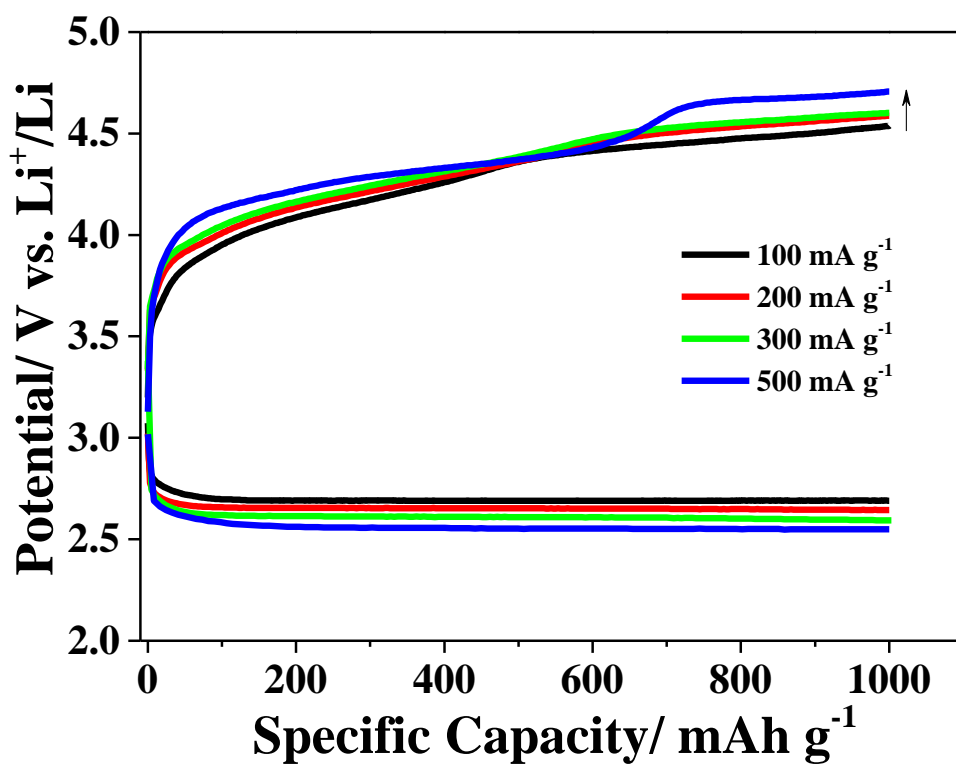


Figure S3. Rate capability of Super P cathodes without the soluble redox mediator MPT in the 1.0 M LiCF₃SO₃/TEGDME electrolyte at different current densities from 100 mA g⁻¹ to 500 mA g⁻¹. The charge voltages are increased with current densities. And the overhigh OER voltage at high rates usually results in the decomposition of organic electrolyte.

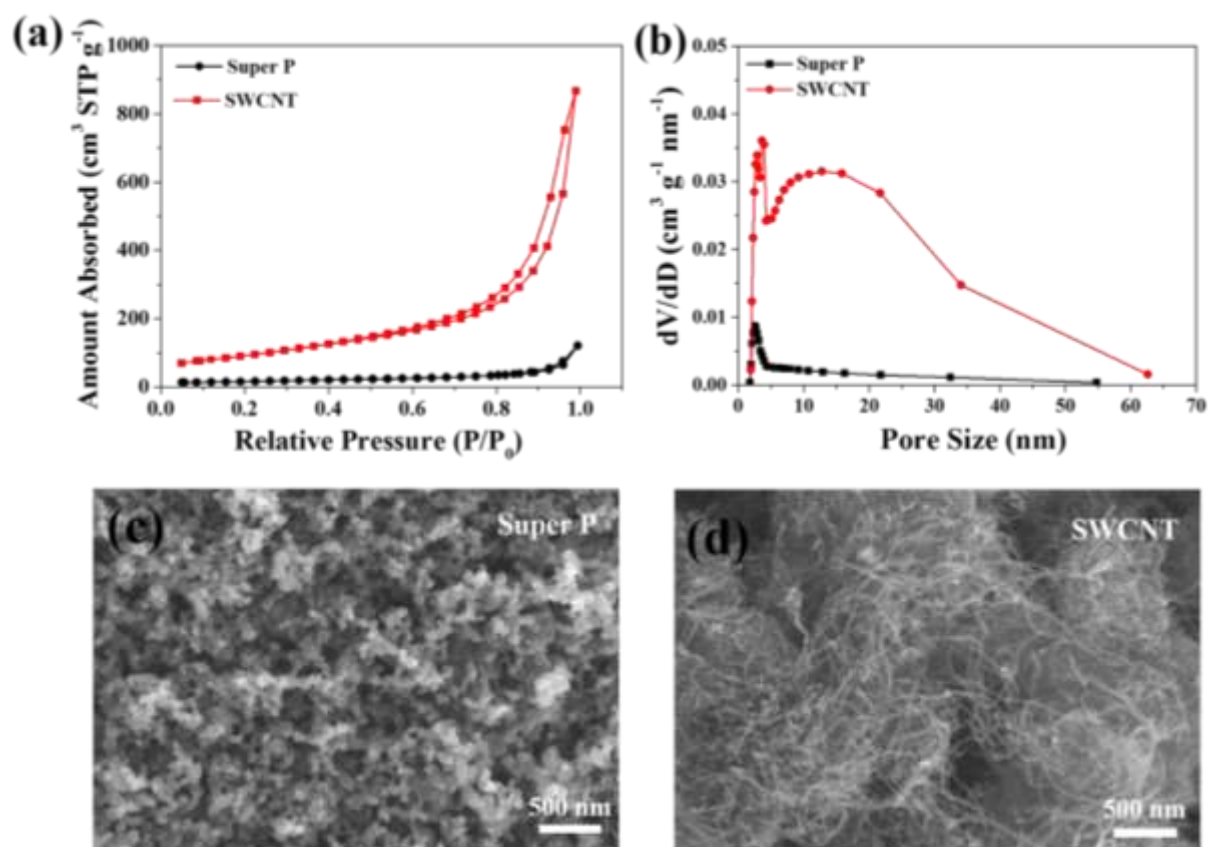


Figure S4. Structure and morphologies characterization of different carbon materials (Super P, and SWCNT). (a) Nitrogen-adsorption-desorption isotherms; (b) BJH pore size distributions; (c) and (d) SEM images, respectively.

Comparison of the capacity obtained with the MPT/MPT⁺ with that obtained for Li-O₂ batteries (the quantity relationship between MPT and Li₂O₂)

In our cells with the MPT/LiCF₃SO₃/TEGDME electrolyte, the maximum number of moles of MPT⁺ formed by oxidizing MPT was 2.0×10^{-5} mol. And the electrical charge was 1.93 C, i. e., 0.54 mAh. It will give 5400 mAh/g_{carbon} at most if the MPT⁺ cations don't react with the discharge product Li₂O₂ and just provide the charge capacity in Li-O₂ cells. However, we demonstrated that those studied Li-O₂ cells with MPT can maintain more than 6 cycles. This indicates that MPT can be recycled in the continuous discharge-charge process.

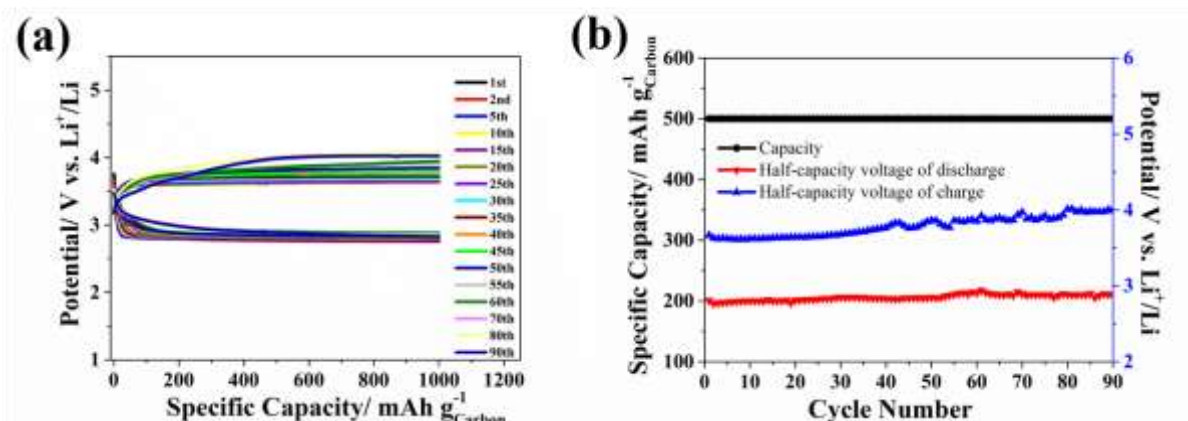


Figure S5. (a) Cycling stability of a Li-O₂ coin cell that employ LiFePO₄ anodes in a 0.1 M MPT/1.0 M LiCF₃SO₃/TEGDME electrolyte with SWCNT cathode at capacity limits of 1000 mAh g⁻¹_{carbon} and a current density of 150 mA g⁻¹. The potentials against Li⁺/Li are converted from LiFePO₄. (b) The relationship between the half-capacity voltage and the cycled numbers during the continuously cycled discharge-charge performance.

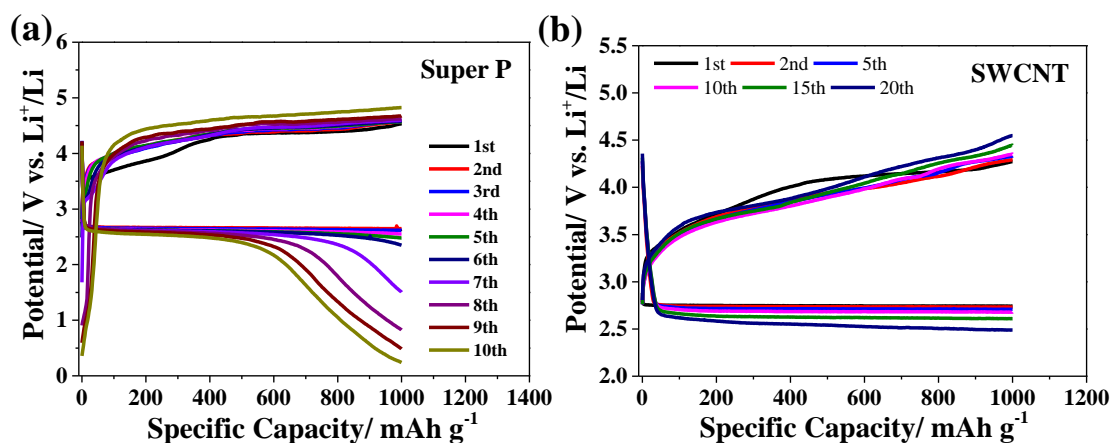


Figure S6. Cycling stability of Li-O₂ coin cells in the absence of MPT with different cathodes: Super P (a); SWCNT (b), at capacity limits of 1000 mAh g⁻¹_{carbon} and a current density of 150 mA g⁻¹. The data shows that both of the charging potential of these two cells are above 4.0 V. And the high charging voltage shall be detrimental to the cycling stability of Li-O₂ cells.

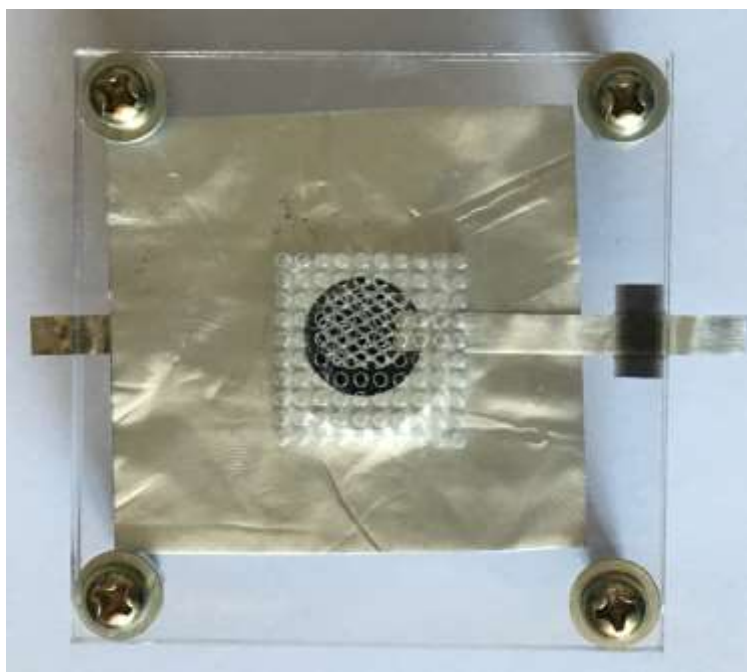


Figure S7. Photograph of a pouch-shaped Li-O₂ cell with the redox mediator MPT in TEGDME-based electrolyte, a SWCNT-coated carbon paper cathode, a solid ceramic electrolyte LAGP film and Li anode.

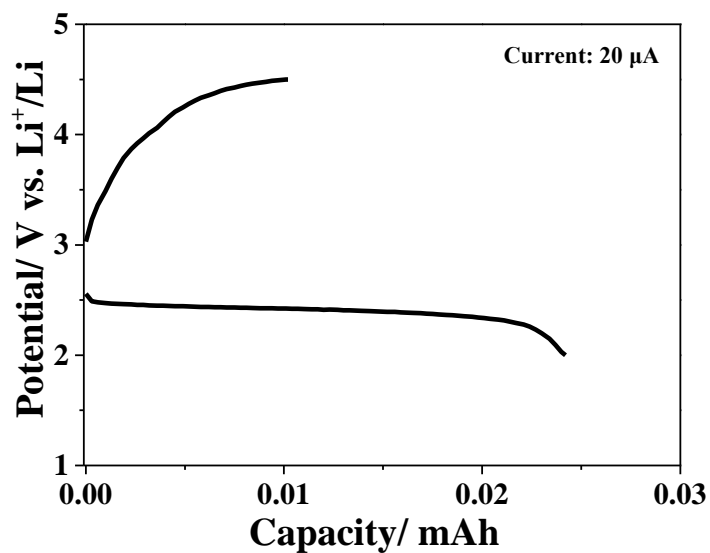


Figure S8. Galvanostatic charge-discharge profile of a Li-O₂ cell only with carbon paper cathode cycled in a 1.0 M LiCF₃SO₃/TEGDME electrolyte at a current of 20 μA and in the potential window of 2~4.5 V. The data shows that carbon paper itself has negligible contribution to cell performance.

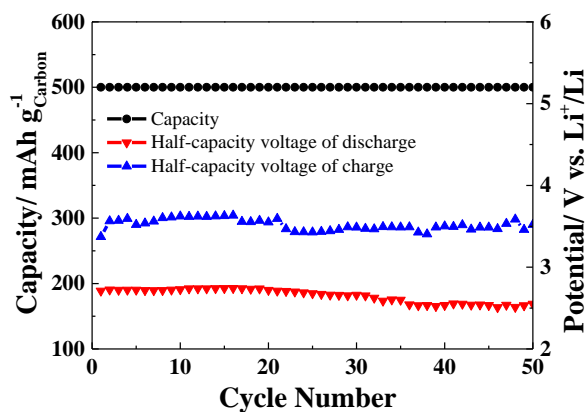


Figure S9. Voltage plots upon cycling of a LAGP-based pouch Li-O₂ battery that employ Li anode in a 0.1 M MPT/1.0 M LiCF₃SO₃/TEGDME electrolyte with SWCNT cathode. This results implied the practical feasibility of Li-O₂ battery system with redox mediators.