Electronic Supplementary Information (ESI)

Porous perovskite $CaMnO_3$ as electrocatalyst for rechargeable Li-O_2 batteries

Xiaopeng Han, Yuxiang Hu, Jingang Yang, Fangyi Cheng,* and Jun Chen*

Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), College of Chemistry, Collaborative Innovation Center of Chemical Science and Engineering, Nankai University, Tianjin 300071, China. Fax: 86-22-23509571, Tel: 86-22-23504482

(F. Cheng) E-mail: fycheng@nankai.edu.cn; (J. Chen) E-mail: chenabc@nankai.edu.cn

Experimental Section

Material Synthesis. Porous perovskite $CaMnO_3$ was synthesized using the citrate gel process. Typically, $Ca(NO_3)_2{\cdot}4H_2O$ and $Mn(NO_3)_2$ with molar ratio of 1:1 was firstly dispersed in distilled water. After dissolved completely, critic acid and ethylene glycol were added to the solution. The water was removed at 85 °C for several hours to form a gel and then dried in vacuum at 80 °C overnight. The gel was heated at 400 °C for 2 h and then at 900 °C for 3 h in Air with a heating rate of 5 °C /min.

Materials characterization. Powder X-ray diffraction (XRD) analysis was characterized by a MiniFlex600 X-ray generator with a Cu Kα radiation. Fourier Transform Infrared (FTIR) spectroscopies were collected on a FTIR-650 spectrometer (Tianjin Gangdong) with a resolution of 2 cm^{-1}. Morphology structures were analysed using scanning electron microscopy (SEM, JEOL JSM7500F), and transmission electron microscopy (TEM, Philips Tecnai F20, 200 kV), Brunauer-Emmett-Teller (BET) surface area was measured using N2 adsorption-desorption at 77 K on a BELsorp-Mini instrument.

Cell assembly. The non-aqueous Li-O_2 cells were prepared using 2023-type coin cell. All the cells were packaged in an argon-filled glove box. The electrochemical batteries were composed of a lithium metal anode, a glass fiber

separator, an air electrode, and electrolyte containing 1 M LITFSI (lithium bis-(trifluoromethanesulfonyl)-imide) in TEGDME (tetraethylene glycol dimethyl ether) dried by molecular sieve. The air electrodes were prepared by casting a mixture of 30 wt% catalyst + 70 wt% Vulcan carbon XC-72 + 10 wt% polytetrafluoroethene (PTFE) or 90 % Vulcan carbon XC-72 + 10 wt% PTFE onto a nickel foam current collector. After completing assembling, the batteries were transferred to a sealed glass container filled with high-purity oxygen.

Electrochemical Measurements. Electrochemical performance of the cells were conducted in 1 atm O_2 at room temperature after a 5 h rest period using a LAND-CT2001A battery-testing instrument. The specific capacity and current density were based on the amount of carbon used into the catalysts. The cyclic voltammograms (CVs) were carried out within 2.0–4.6 V at room temperature on parstat 263A workstation (AMETEK). The electrochemical impedance spectroscopy (EIS) was performed using Parstat 2273 potentiostat/galvanostat workstation (AMETEK) at a frequency range of 100 kHz to 100 mHz.

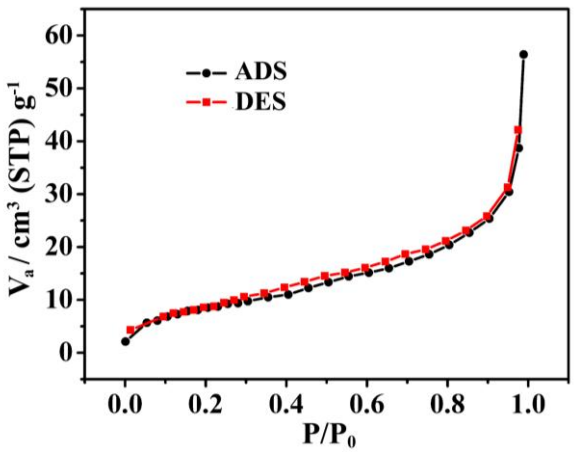

Fig. S1 Nitrogen adsorption and desorption isotherms at 77 K for as-prepared porous $CaMnO_3$.

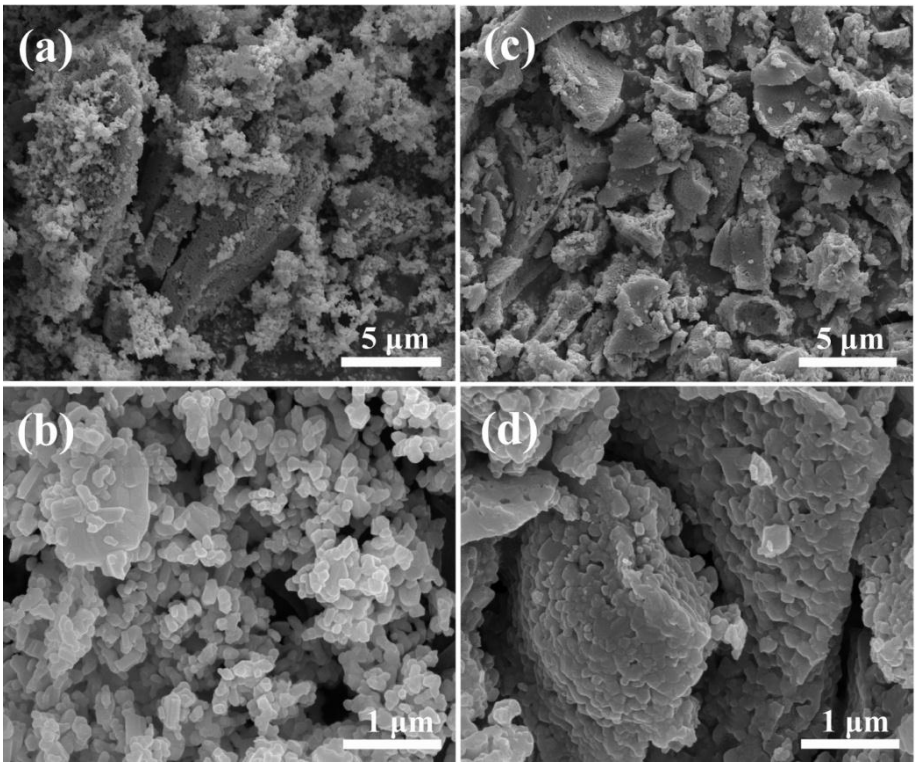

Fig. S2 Prepared $CaMnO_3$ with different molar ratio of critic acid to total metal cations: (a,b) 2:1 and (c,d) 3:1.

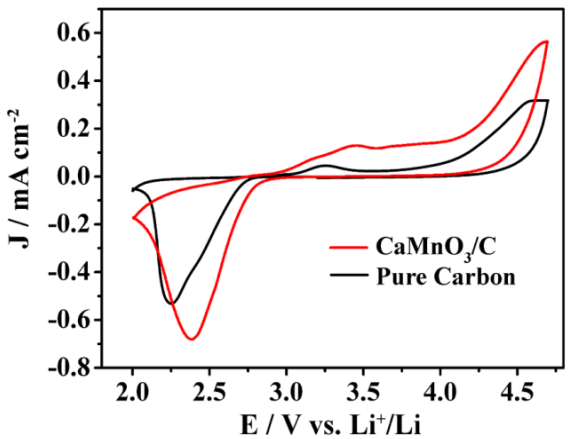

Fig. S3 CV curves of $CaMnO_3$/C and carbon-only electrode at a scan rate of 0.1 mV/s.

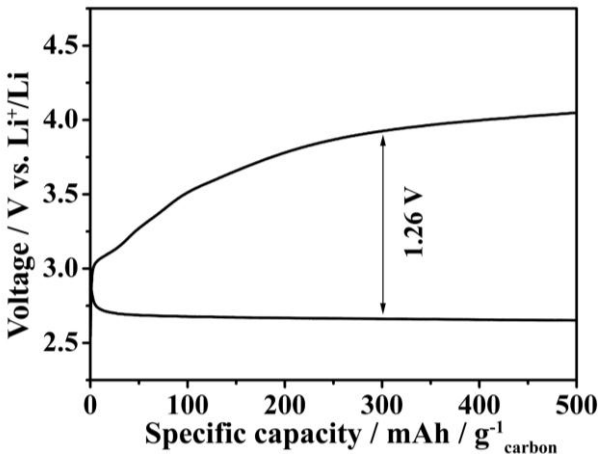

Fig. S4 Discharge/charge curves of Pt/C cathode at a current density of 50 mA g^{-1}_{carbon} with controlled capacity of 500 mAh g^{-1}_{carbon}.

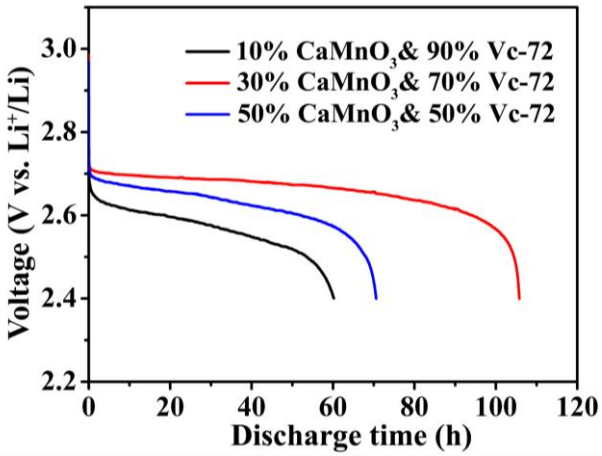

Fig. S5 Influence of different amount of conductive carbon additives on the discharge performance of assembled Li-O_2 batteries at a current density of 50 mA/g^{-1}_{carbon}.

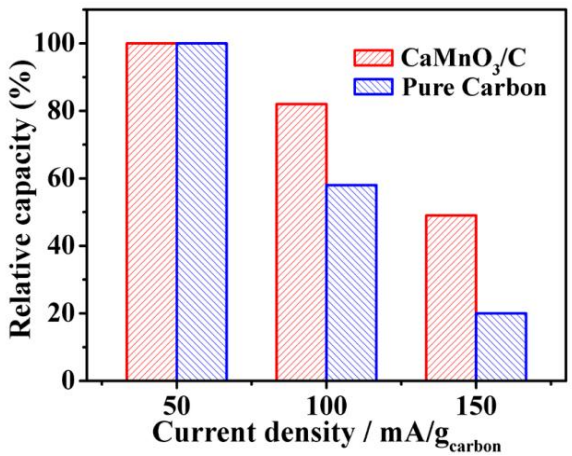

Fig. S6 Relative discharge capacities at different current densities of $CaMnO_3$/C and carbon-only batteries.

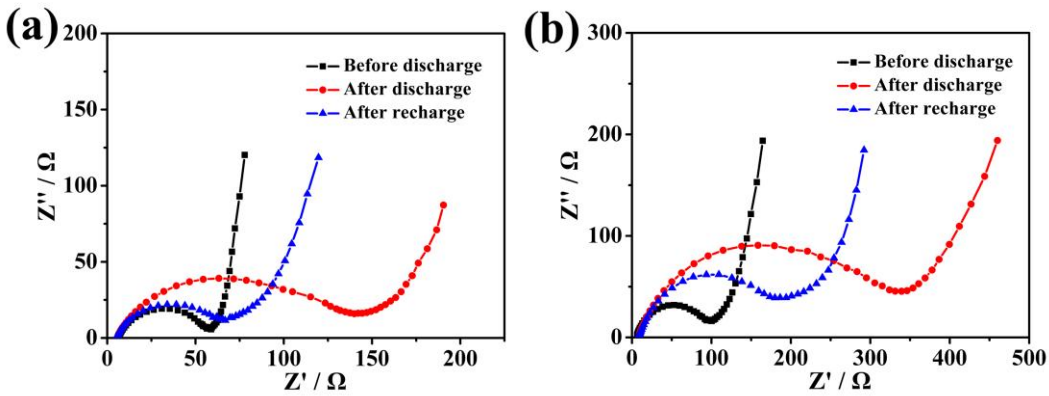

Fig. S7 Electrochemical impedance spectroscopy measurements of $CaMnO_3$/C (a) and carbon-only (b) electrodes at different discharge/recharge states.

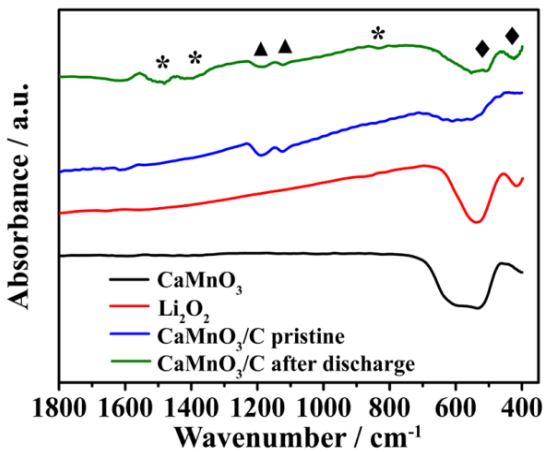

Fig. S8 FTIR spectroscopy of pristine and discharged (2.0 V) $CaMnO_3$/C-based electrode. The neat $CaMnO_3$ and Li_2O_2 are listed for comparison. The signals of Li_2O_2, Li_2CO_3 and PTFE are marked by ◆, * and ▲, respectively.

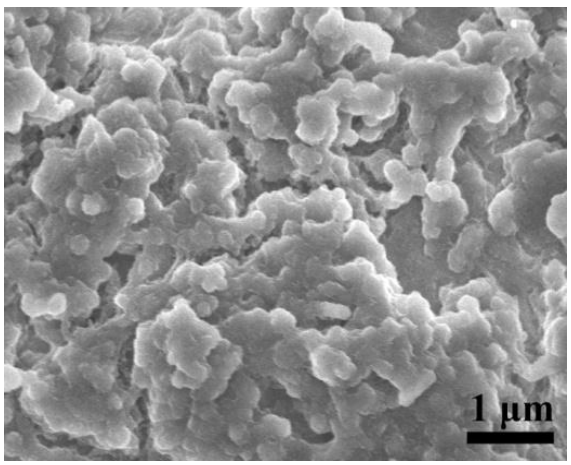

Fig. S9 SEM image of the carbon-only electrode after charging.