

Electronic Supporting Information (ESI)

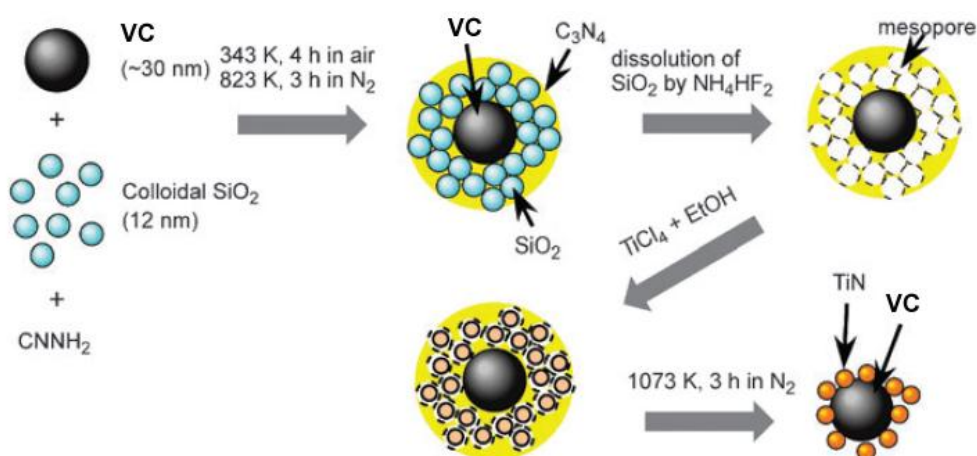
Carbon Supported TiN Nanoparticles: An Efficient Bifunctional Catalyst for Non-Aqueous Li-O₂ batteries†

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Experimental

Assembly of Li-O₂ batteries

The preparation of n-TiN supported on Vulcan XC-72 (n-TiN/VC) with a weight percentage of 30 wt% was depicted in Scheme S1 and described in Ref. 8 via a template method. The m-TiN/VC sample was obtained by directly grinding the commercially available micro-sized TiN and VC particles in a mortar with a weight ratio of 3 to 7.



Scheme S1 Preparation process of n-TiN/VC.

Triglyme (G3, Wako) was dried with 4Å molecular sieves before use. Lithium bis(trifluoromethylsulfonyl)amide (LiTFSA, Wako) was used as received. The electrolytes were prepared by dissolving LiTFSA in G3 with a molar ratio of 1:5 in a glovebox filled with argon ($[\text{H}_2\text{O}] < 1 \text{ ppm}$ and $[\text{O}_2] < 1 \text{ ppm}$). A lithium foil was put in the as-prepared electrolyte to eliminate any residual H_2O and CO_2 . Li- O_2 battery was assembled in a coin cell with 7 holes exposed to O_2 (purity, 99.9 %) on the cathode side. It was comprised of a Li metal anode, an electrolyte impregnated in a glass fiber filter separator (Whatman), and a porous cathode. The porous cathode was prepared by coating a paste of cathode material (VC, m-TiN/VC, and n-TiN/VC) and polyvinylidene fluoride (PVDF) with a weight ratio of 90/10 in N-methyl-2-pyrrolidone (NMP) onto a carbon paper ($\Phi = 10 \text{ mm}$, Type GDL 35 BA, SIGRACET Gas Diffusion Media). The loading of VC in a cathode was between 0.3 mg/cm^2 and 0.5 mg/cm^2 .

Characterization and measurements

Scanning electron microscope (SEM) and transmission electron microscope (TEM) were obtained on Hitachi S4800 and JEOL JEM-2100, respectively. Powder X-ray diffraction (XRD) was performed to characterize the discharge and recharge products on a Bruker D8 Advanced diffractometer with $\text{Cu K}\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation. The XRD samples, discharged/recharged electrodes were taken out from a coin cell, washed with dimethoxyethane, and wiped with filter papers. The samples were enclosed with a thin transparent polymer film to reduce their exposure to air during testing. The employed step was 0.02° , and the step duration is 1 s. The continuous scan range of 2θ is from 30° to 80° . The Brunauer-Emmett-Teller (BET) surface area was conducted on Belsorp 18 via nitrogen adsorption-desorption. Fourier transform infrared (FTIR) measurements FTIR were obtained on a JASCO instrument of FT/IR-6200 from 2000 to 400 cm^{-1} with a resolution of 2 cm^{-1} .

The cyclic voltammograms (CVs) of Li- O_2 batteries were conducted at a scan rate of 0.1 mV/s from 2.4 to 4.0 V in O_2 atmosphere. The samples, VC, m-TiN/VC, and n-TiN/VC, for linear sweep voltammograms (LSVs) were prepared as the processes

of Li-O₂ batteries, and they were examined from their open circuit voltages to 5.1 V at 0.1 mV/s in O₂ atmosphere. Galvanostatic discharge/charge was conducted on a Hokuto discharging/charging system. All the electrochemical measurements were conducted at 25 °C and in 1 atm of O₂ flow. Both of the current density and specific capacity were based on the unit mass of VC carbon black employed in the catalyst layer.

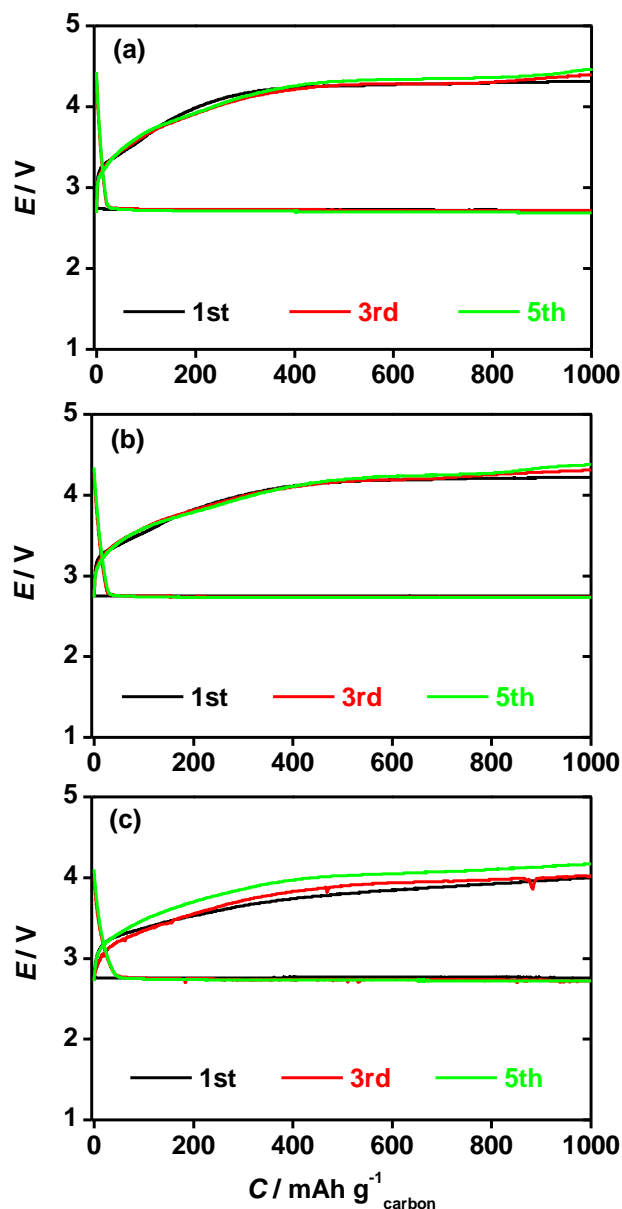


Fig. S1 Cycling performance of Li-O₂ batteries with VC (a), m-TiN/VC (b), and n-TiN/VC (c) as cathode catalyst, respectively.

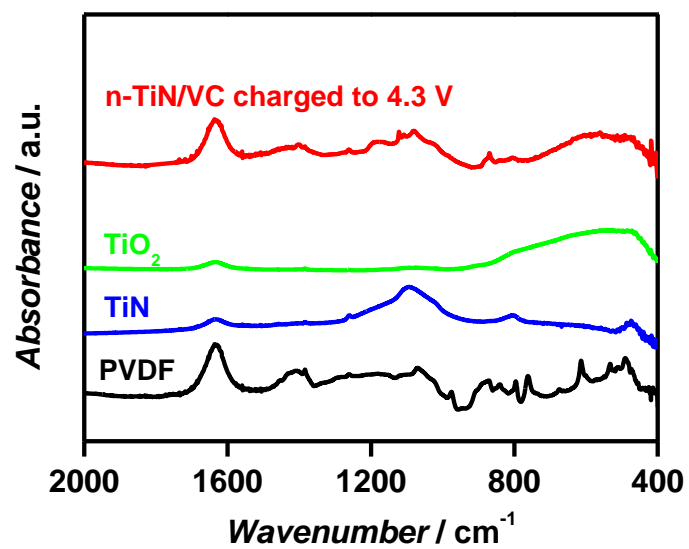


Fig. S2 FTIR spectra of standard PVDF, TiN, TiO₂, and the electrode n-TiN/VC recharged to 4.3 V.