Titanium Nitride catalytic cathode in a Li-air fuel cell with acidic aqueous solution

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Electronic Supplementary Information (ESI)

1, Experimental method

*Preparation of catalyst layer and gas diffusion layer-* The air catalytic electrode includes a catalyst layer and a gas diffusion layer. TiN employed for catalytic active material was purchased from Wako Corp. The catalyst layer can be prepared as following procedures. TiN (80 wt.%), carbon black (10 wt.%) and polytetrafluoroethylene (PTFE) (10 wt.%) were well mixed, and then was roller-pressed into a sheet to form catalytic layer. The gas diffusion layer was prepared by mixing acetylene black (60 wt.%) and PTFE emulsion (40 wt.%) with isopropanol into paste and then rolling the paste into a film. The air catalytic electrode was finished by pressing the catalyst layer and gas diffusion layer onto a titanium mesh. Note that all the surface of titanium mesh is covered with catalyst layer. The area of the air electrode was 1 cm^2, and the mass load of catalyst layer was 5 mg cm^{-2}. While sufficient for the characterization of prototype lithium-air fuel cell, the catalyst layer loading should certainly be increased in case of practical development.

Electrochemical performance test- The electrochemical property of TiN based catalyst layer was investigated by test of electrochemical polarization curves using a classic three-electrode cell. TiN based catalyst layer pressing onto a titanium mesh was used as a working electrode. An activated carbon (AC) negative composite electrode and saturate calomel electrode (SCE, 0.242 V vs. normal hydrogen electrode) were used as counter and reference electrodes. The negative composite electrode was prepared by the same method as the catalyst layer described above. It consists of 85 wt % activated carbon (AC), 10 wt % AB, and 5 wt % PTFE. The aqueous electrolytes employed here consisted of LiAc saturated 90 vol% HAc solution (pH=3.65). The polarization curves tests were controlled at a scan rate of 5 mV s^{-1}. This series of experiments were conducted with Solartron Instrument Model 1287 controlled by a computer at 25°C.

Electrochemical tests were performed using a Solartron 1287 Electrochemical Interface and a Solartron 1255B Frequency Response Analyzer, and controlled by Corrware and Z-plot from a PC. For the Electrochemical impedance spectra (EIS) test metallic lithium was used as the counter and reference electrode. The frequency limits were typically set between 1000 kHz to 0.01 Hz. The DC cell voltage was kept at the OCV and AC oscillation was 10 mV. The obtained data of EIS were fitted from equivalent circuit using Zview 2.70 software.

Characterization of structure and morphology- Powder X-ray diffraction (XRD) data for the sample was collected with a Bruker D8 Advanced diffractometer using Cu Kα (λ=1.5406 Å) radiation. The morphology of TiN was characterized via field-emission scanning electron microscopy (FESEM, LEO Gemini Supra 35). The Brunauer-Emmett-Teller (BET) specific surface area measurement of the TiN particles was carried out on a Belsop 18 using nitrogen adsorption-desorption method after degassing the powder sample at 150 ℃ for 8 h in vacuum.
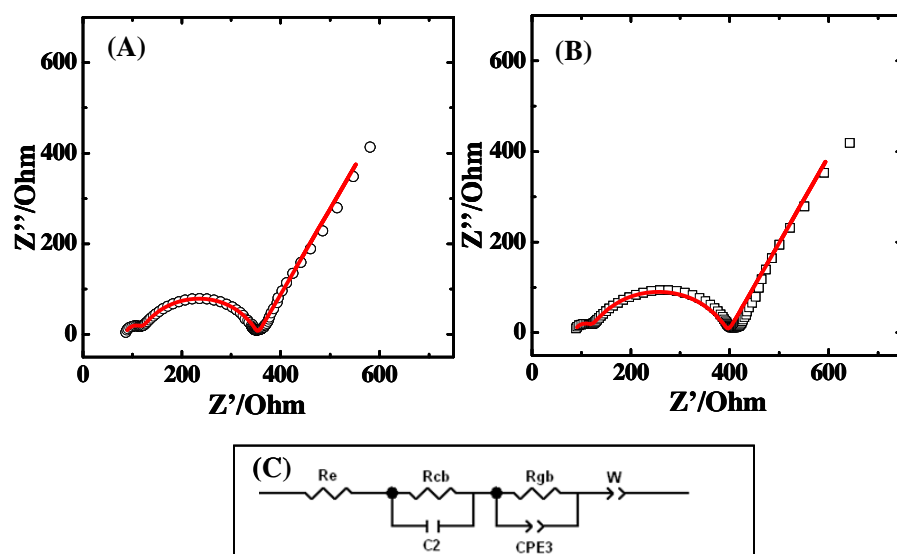
2, Supplementary data
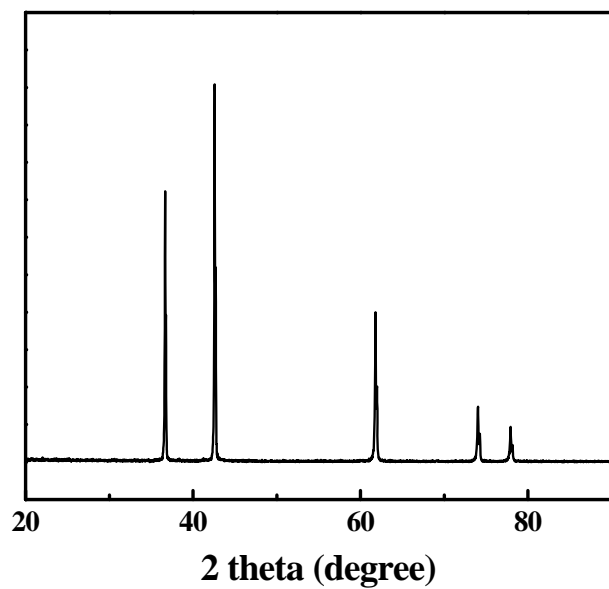
Fig. S1. XRD parttern of TiN powder.
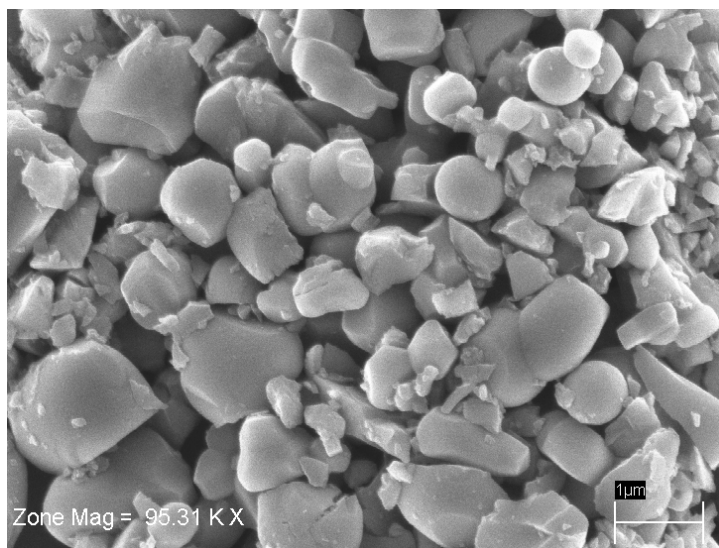
Fig. S2 FE-Scaning electron microscopy of TiN powder.

Fig. S3. Nyquist plots of the Li-air fuel cell combining TiN catalyst in the hybrid electrolyte at OCV. (A), Before discharge test. (B), After 200 hours discharge. (C) equivalent circuit used to fit the experimental data.