Electronic Supplementary Information (ESI):

Natural eggshell membrane as separator for improved Coulombic efficiency in air-cathode microbial fuel cell

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Separation of eggshell membrane (ESM)

The waste ESM was rinsed in 0.1 M HCl for 2 minutes to etch the $CaCO_3$ eggshell, so that the ESM was easily separated from the outer eggshell by the space filled with CO_2. The ESM washed with deionized (DI) water thoroughly was directly used as separator in the air-cathode MFC.

MFC reactor construction and operation

Cubic-shaped single-chamber MFC reactor (28 mL, 4 cm long cylindrical chamber) was made up with an anode of carbon brush and an open−to−air cathode (7 cm^2 with 0.5mg/cm^2 Pt catalyst loading) placed on the opposite side of Plexiglas tube at a fixed external circuit resistance of 1000 Ω. The gas diffusion layers (GDLs) were prepared by rolling carbon black with poly (tetrafluoroethylene) (PTFE) (60 wt%) with a mass ratio of 7:3, and the Pt/C catalysts were dispersed with PTFE with a mass ratio of 6:1 as reported.[1] The ESM separator was placed against cathodes and all MFC tests were conducted at 30 °C.

MFC was inoculated using 14 mL effluent from reactors operated for 3 months and 14 mL growth medium, which contains NH_4Cl (0.31 g/L), $NaH_2PO_4•2H_2O$ (3.32 g/L), $Na_2HPO_4•12H_2O$ (10.32 g/L), KCl (0.13 g/L), vitamins (5 mL/L), trace minerals (12.5 mL/L), and glucose (1 g/L). Reactors were operated in fed-batch mode, and substrates were replaced when voltage is

lower than 50 mV. All tests were conducted at least three duplicates, with average values (±S.D.) of duplicates given in the text. Only one of these duplicates was shown in the figures for clarity.

Characterizations

Scanning electron microscopy (SEM) images were obtained using a field emission scanning electron microscope (Guanta 200F, FEI, U. S.) Fourier transform infrared spectroscopy (FT-IR, Spectrum GX, Perkin Elmer, U. S.) was used to identify the functional groups of ESM. The polarization and power density curves were obtained using linear sweep voltammetry (LSV). Before tests, the MFC reactors were completely refilled with fresh medium and left at the open circuit for 1h. The test was conducted from open circuit voltage (OCV) to 0 V *vs.* the cathode potential at a scan rate of 1 mV/s. Current density and power density normalized to the cathode surface area (A/cm^2 and W/m^2) were calculated from $j=I/A$ and $P=IU/A$. LSV was also performed to examine the cathode electroactivity with the working electrode of Pt/C-ESM, and Pt/C filled with 50 mM PBS solution mentioned above, the 1 cm^2 platinum foil square counter electrode, and the saturated calomel electrode (SCE, +0.248 V *vs.* SHE) reference electrode. Electrochemical impedance spectroscopy (EIS) was conducted over the frequency range of 100000 Hz to 0.01 Hz with a sinusoidal perturbation of 10 mV. The oxygen mass transfer coefficient was calculated by measuring the change in dissolved oxygen concentration over time as previously reported.[2]

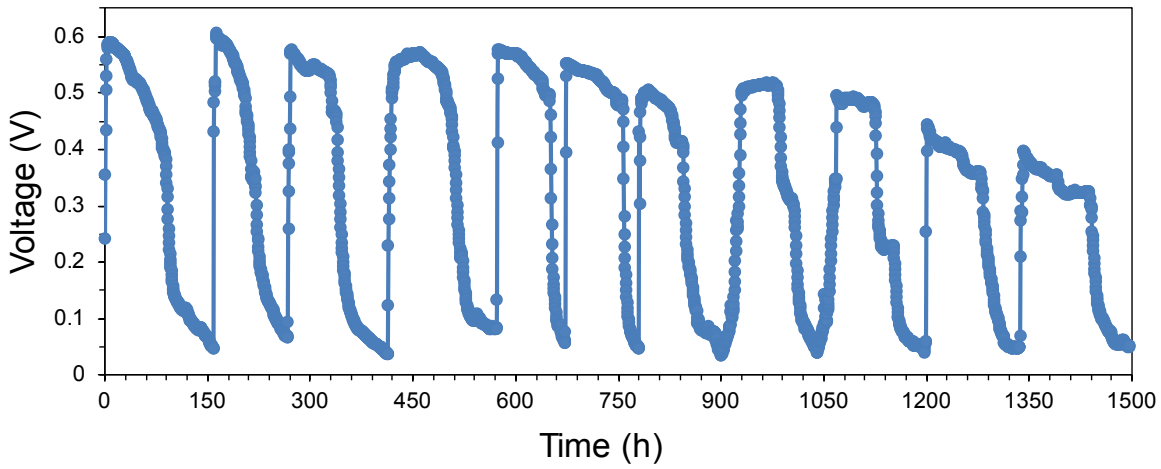

Fig. S1. Voltage output as operation continues for the cathode with ESM.

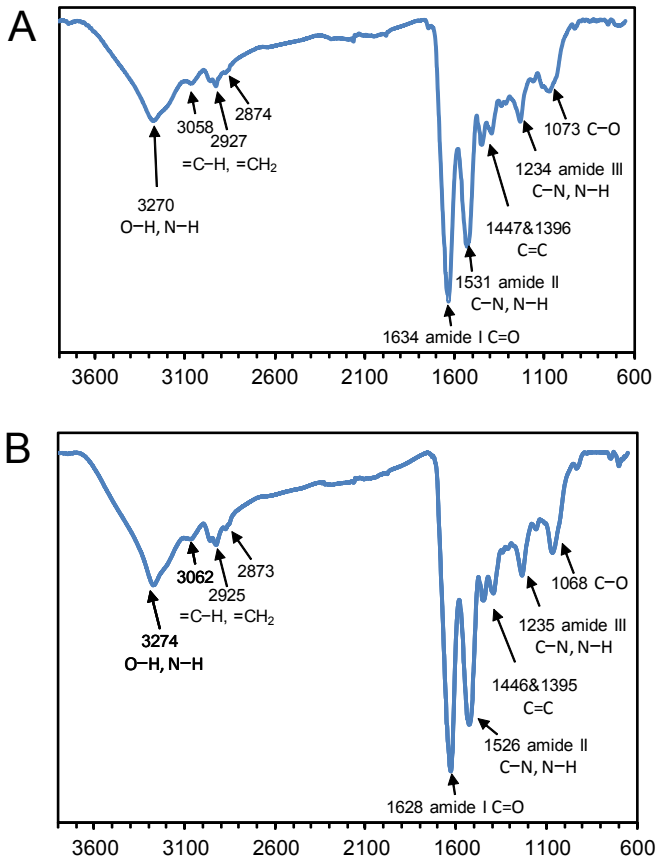

Fig. S2. The FT-IR spectra of ESM before and after operation.

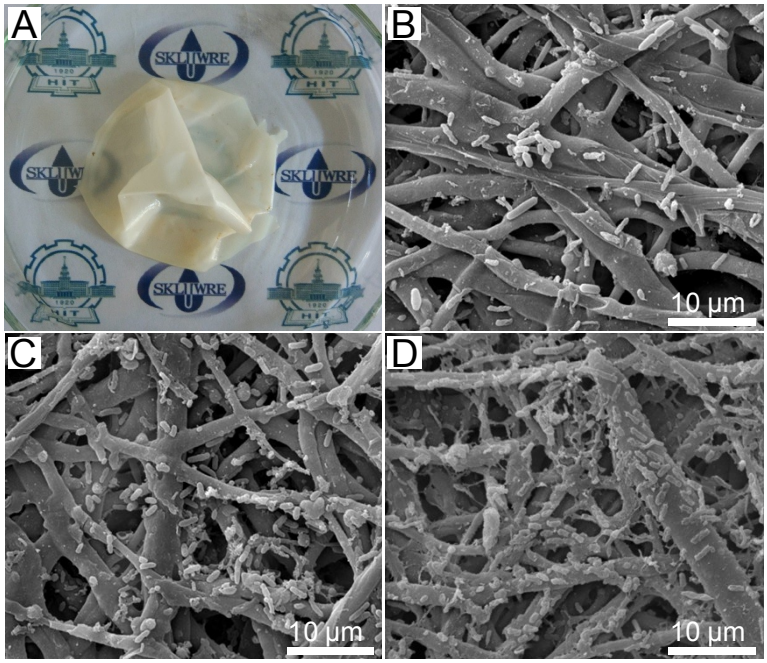

Fig. S3. (A)The optical image of EMS after 11 cycles' operation, and corresponding SEM images after the 4th cycle (B), 9th cycle (C), and 11th cycle (D).

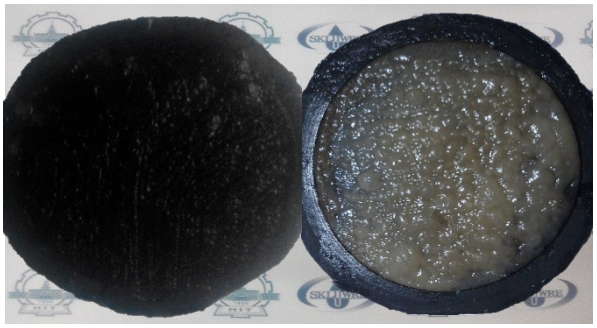

Fig. S4. Optical images of the air-cathode of MFC after long-term operation in the presence (left) and absence (right) of ESM.

References

1. M. Ma, S. You, X. Gong, Y. Dai, J. Zou, H. Fu, *J. Power Sources*, 2015, **283**, 74-83.

2. J. R. Kim, S. Cheng, S. -E. Oh, B. E. Logan, *Environ. Sci. Technol*., 2007, **41**, 1004-1009.