Supporting Information

Effects of the Electrode Wettability on the Deep Discharge Capacity of Li−O_2 Batteries.

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S1. Electrical Resistance Measurement

The Electrochemical Impedence Spectroscopy (EIS) is applied to carry out electrical resistance measurement on Li−O_2 batteries with customized electrodes of various wettability. The Nyquist plots of fitted data using the equivalent circuit is shown in Figure S1. The equivalent circuit includes an ohmic resistance (R_1), which considers the electronic resistance of the electrodes, current collectors, and ionic resistance of the electrolyte, as well as the contact resistance between these components. R_2 and R_3 are due to the charge transfer resistance and mass transfer resistance at the two electrodes. The diagonal line at low frequencies represents the Warburg impedance (W_4), which is due to the diffusion impedance of the oxidant and reductant. C_2 and C_3 denote the double layer capacitance formed when a non-conducting media separates two conducting electrodes. Due to the same configuration of Li−O_2 batteries, the variations of R_1 can be attributed to the electrode resistance which is dominated by the ionic resistance.

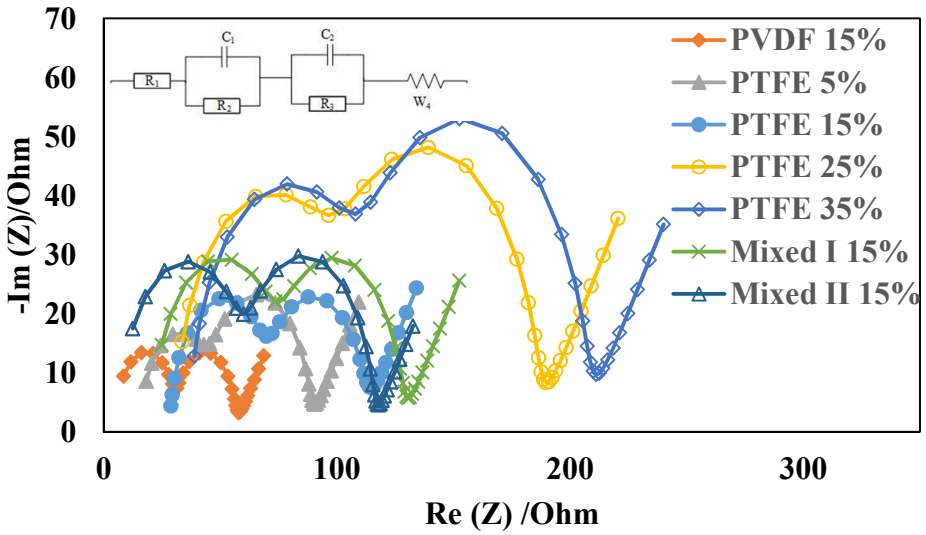
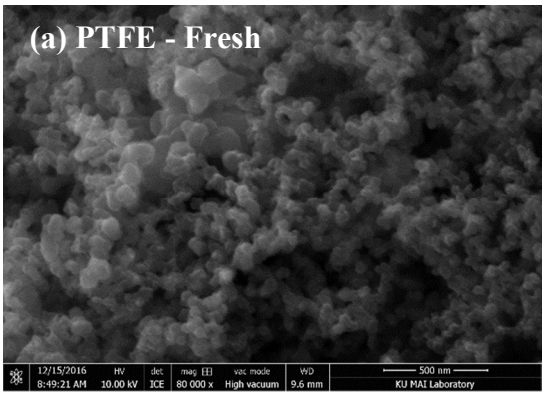
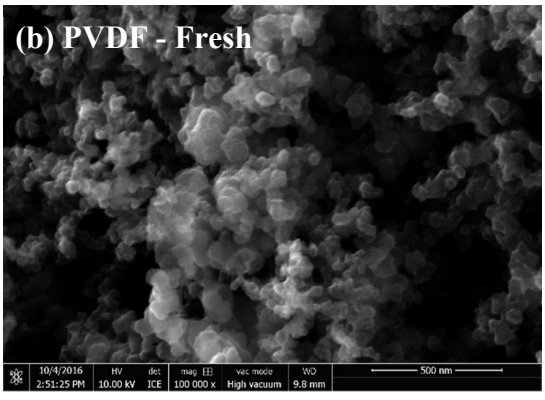


Figure S1. Nyquist plots of batteries with customized electrode with different wettability. The point are simulated data obtained using the equivalent circuit shown in this plot.

S2. Scanning Electron Microscope (SEM) Measurement After Discharge.

The SEM images of customized electrode with 15% PTFE carbon coatings and with 15% PVDF carbon coatings discharged with the specific capacity of 1000mA h g^{-1} are scanned using FEI Versa 3D Dual Beam. The SEM scanning on O_2-facing side of the discharged customized electrode with 15% PTFE and with 15% PVDF carbon coatings are shown in Figure S2. Comparing the SEM images of electrode before and after discharge, it is found that solid products accumulated and blocked the O_2 diffusion path after discharge, which limits the specific discharge capacity eventually. The pores of lyophilic electrode are filled with more solid products at the side facing O_2 while the solid products deposition is reduced and the sizes of unblocked pores are larger in the lyophobic electrode. The Li−O_2 battery with lyophobic electrode can provide more O_2 diffusion path and thus achieve a much higher specific discharge capacity. Quantitative analyses on porosity and pore size distribution are performed on SEM images of Fig. S1 (c) and (d) by ImageJ[1-2]. The porosity of the discharged electrode with 15% PTFE is 16.05% while the other electrode has smaller porosity of 8.02%. The pore size distributions of these two electrodes from Figure S3 shows that most pores were in the range of 0-20 nm. The electrode with 15% PTFE reserved more mesopores (2-50 nm) result in a larger porosity and are unblocked space for O_2 diffusion.





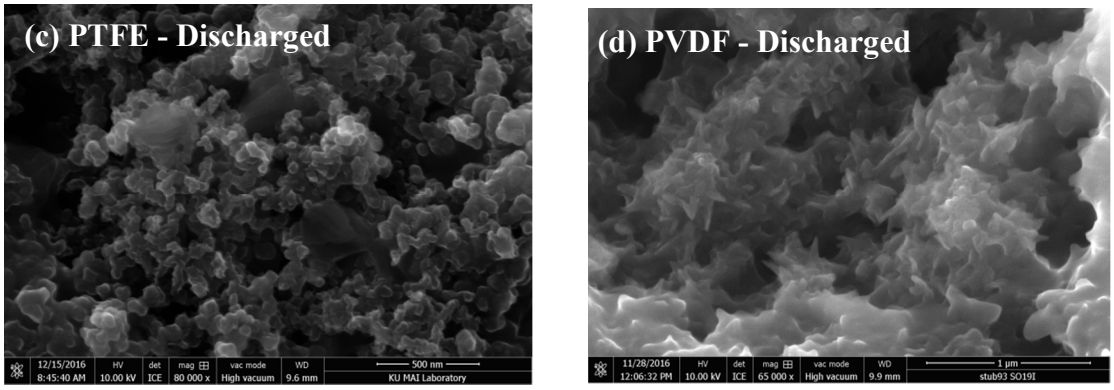


Figure S2. SEM measurement on fresh electrodes with (a) 15% PTFE, (b) 15% PVDF and discharged electrode with (c) 15% PTFE and (d) 15% PVDF at the cut-off specific capacity of 1000 mA h g^{-1}.

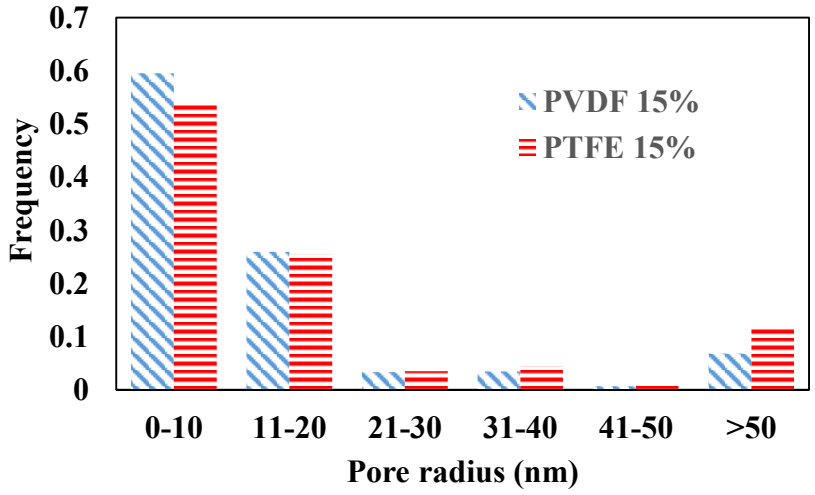


Figure S3. Pore size distribution analysis of SEM image on discharged electrode with 15% PTFE and 15% PVDF carbon coatings.

S3. Discharge-charge Curves

The Li-O_2 batteries with PTFE 15% electrode was cycled with cut-off capacity of 1000 mAh/g. The discharge-charge curves are shown in Figure S4. The over-potential of the 1st cycle is slightly higher than other cycles but the coulombic efficiency drops significantly after the 12th

cycle. After 14th cycle, the coulombic efficiency drops below 60% and therefore the cycle test is terminated.

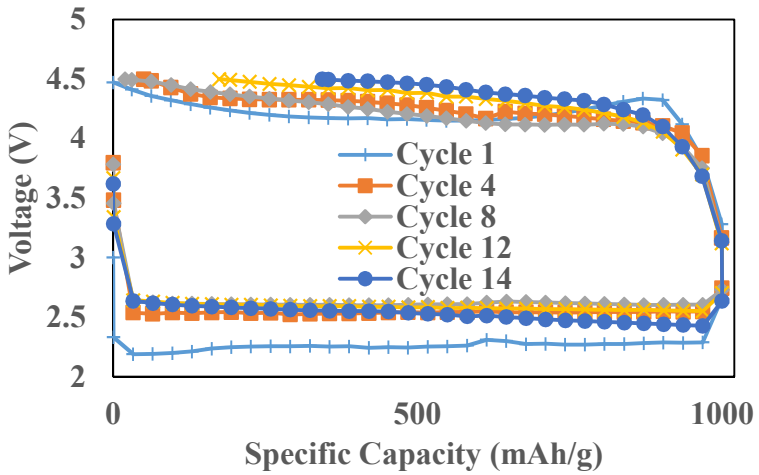


Figure S4. The cycling curves of Li−O_2 batteries with PTFE 15% electrode.

Reference

1. Belwalkar, A.; Grasing, E.; Van Geertruyden, W.; Huang, Z.; Misiolek, W., Effect of processing parameters on pore structure and thickness of anodic aluminum oxide (AAO) tubular membranes. *J. Membr. Sci.* **2008,** *319* (1), 192-198.

2. Latief, F. In *Analysis and Visualization of 2D and 3D Grain and Pore Size ofFontainebleau Sandstone Using Digital Rock Physics*, Journal of Physics: Conference Series, IOP Publishing: 2016; p 012047.