Electronic Supporting Information (ESI)

Low Charge Overpotentials in Lithium-Oxygen Batteries Based on Tetraglyme Electrolytes with Limited Amount of Water†

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Experimental Section

Materials

$RuCl_3 \cdot xH_2O$: purity of 36 - 42 wt% based on Ru, Wako Chemicals

Ethylene glycol: purity of > 99.5 %, Wako Chemicals

MnO_2: electrolytic γ-MnO_2 (EMD), TOSOH, Japan

LiOH: anhydrous, > 98 %, Wako Chemicals

Tetraglyme: G4, Tokyo Chemical Industry Co., Ltd, purity of > 98 %

$LiClO_4$: purity of > 99 %, Wako Chemicals

PTFE: a dispersion of 60 wt%, Du Pont-Mitsui Fluorochemicals Co. Ltd

Carbon paper: SIGRACET Gas Diffusion Media, Type GDL 35BA

$LiFePO_4$: Sumitomo Osaka Cement

Glassy fiber filter paper: GF/A, Whatman

Methods

Ru nanoparticles supported on Super P (Ru/SP) were synthesized as following: 15 mg of Ru in $RuCl_3 \cdot xH_2O$ was added to ethylene glycol (EG) containing 170 mg of SP. After stirring overnight, NaOH in EG was slowly added to adjust the pH to 13. The suspension was heated to 160 °C for 3 hrs with flowing N_2 and then its pH was adjusted to 3 with 0.1 M HCl. The resultant suspension was filtered and washed with deionized water until the pH reached about 7. The obtained Ru/SP was dried at 80 °C in a vacuum oven for 12 hrs. For the preparation of EMD and Ru nanoparticles supported on Super P (EMD/Ru/SP), EMD ball-milled to nanometer scale and Ru/SP were firstly dispered in aqueous solution with a weight ratio of EMD : Ru : SP = 7.5 : 7.5 : 85. After sonicated for 30 min and then stirred for 2 hrs, the suspension was filtered and the product EMD/Ru/SP was dried at 80 °C under vacuum for 12 hrs. EMD/SP with a weight ratio of EMD : SP = 7.5 : 92.5 was prepared by a similar way. EMD nanoparticles and SP were firstly sonicated in aqueous solution for 30 min and further stirred for 2 hrs. The product EMD/SP was obtained after filtered and dired at 80 °C in a vacuum oven for 12 hrs. For the preparation of LiOH/Ru/SP, LiOH powder was firstly ball-milled and then mixed with Ru/SP with a weight ratio of LiOH : Ru/SP = 30 : 70.

Electrolytes

Tetraglyme (G4) was dried over 4 Å molecular sieves. $LiClO_4$ was dried at 80 °C in a vacuum oven overnight. The dry electrolyte with 0.5 M $LiClO_4$ in G4 was stored in a glove box under Ar atmosphere. The water concentration in the dry electrolyte measured by Karl-Fischer titration is about 11 ppm. Ultrapure deionized water (18.2 MΩ-cm, Millipore) was used for preparing electrolytes with water concentrations of 78 ppm, 1700 ppm and 4600 ppm.

Cathodes

The electrode films composed of EMD/Ru/SP and PTFE with a ratio of 85 : 15wt% were prepared by rolling the paste of EMD/Ru/SP and PTFE solution. Then, the electrode films were pressed onto hydrophobic carbon paper as the cathodes for Li-O_2 batteries. The mass loading of EMD/Ru/SP is about 0.5-1.0 mg cm^{-2}.

The Ru/SP cathodes (Ru/SP : PTFE = 85 : 15 wt%), EMD/SP (Ru/SP : PTFE = 85 : 15 wt%) cathodes and LiOH/Ru/SP cathodes were prepared by the similar way to EMD/Ru/SP cathodes.

Anodes

To avoid any contamination from reactions between a Li metal anode and H_2O, $LiFePO_4$ was employed as the anode. The potential of $LiFePO_4$ is invariant with the state of charge at ~3.45 V. The anode was prepared by rolling the paste consisting of $LiFePO_4$, Super P and PTFE (80 : 15 : 5 wt%), and then the film was pressed onto an Al mesh. The mass loading of $LiFePO_4$ is above 10 mg cm^{-2} to provide excess Li^+. All potentials are reported to against Li/Li^+.

Battery assembly

The amount of electrolytes in a coin cell was 40 μL. Glassy fiber filter paper was employed as separator. The battery assembly was conducted in a 2032 coin cell with holes on the top in an Ar filled glove box (< 0.1 ppm of H_2O and 5 ppm of O_2). The Li-O_2 battery stored in a sealed glass chamber with a volume capacity of 650 mL was purged with O_2 (99.999%) before electrochemical tests.

Measurements and Characterization

All the electrochemical measurements were conducted at 25 °C. Galvanostatic discharge/charge was conducted on a Hokuto discharging/charging system. Cyclic voltammograms were carried out on a Solartron system. The specific capacities and currents are based on the mass of EMD/Ru/SP in cathodes. For *ex-situ* X-ray diffraction (XRD) and scanning electron microscopy (SEM) measurements of the discharged cathodes, discharged batteries were transferred to an argon-filled glove box and the cathodes were extracted and placed in a glass vial. The cathodes were rinsed with DME to wash off the electrolyte salt and then dried in a vacuum chamber for 5 min. The dried cathodes were placed in a home-built X-ray cell sealed with a kapton® polyimide film. XRD measurements were performed on a Bruker D8 Advanced diffractometer with Cu Kα ($\lambda = 1.5406$ Å) radiation with a scan rate of 0.016 °/s. SEM was performed on Hitachi S8000. The dried cathodes were taken to the SEM sample loading chamber in a sealed glass bottle. The time from opening the glass bottle to finishing sample loading into the SEM machine was < 10 seconds.

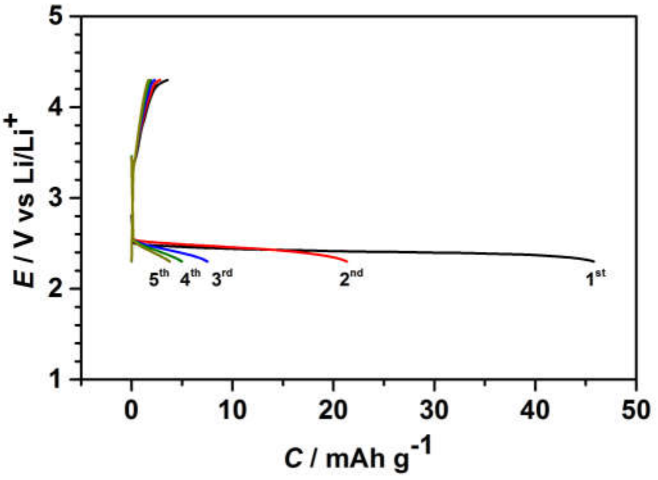

Fig. S1 The discharge and charge profiles of the initial 5 cycles of carbon paper (GDL) of Li-O_2 battery in the dry electrolyte at 0.1 mA cm^{-2}. The contribution of GDL can be negligible because of the low discharge potentials and decaying discharge capacities, and charge failure in the applied potential window.

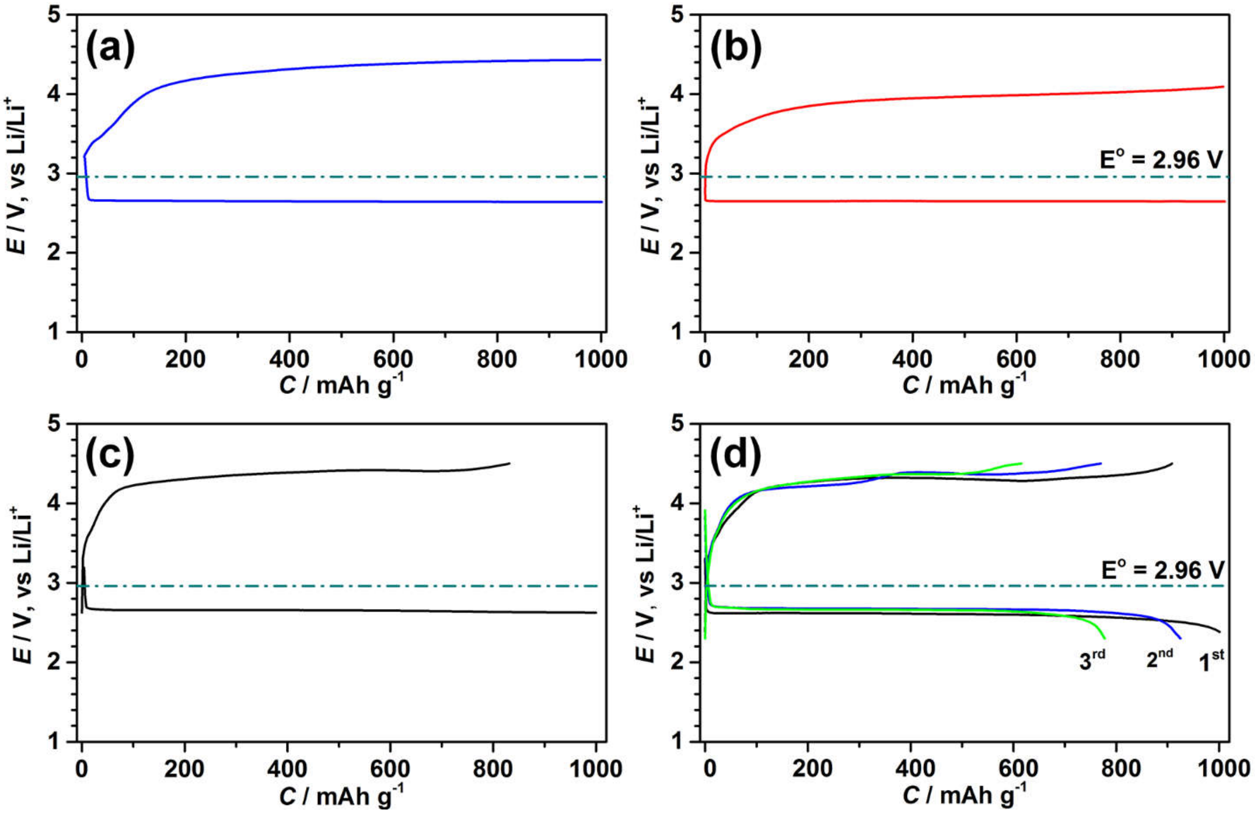

Fig. S2 The discharge-charge profiles of the Li-O_2 batteries with (a) SP and (b) Ru/SP cathodes and the dry electrolyte (~11 ppm of H_2O) at 500 mA g^{-1}. The discharge-charge profiles of the Li-O_2 batteries with (c) SP and (d) EMD/SP cathodes and the electrolyte with 4600 ppm of H_2O at 250 mA g^{-1}.

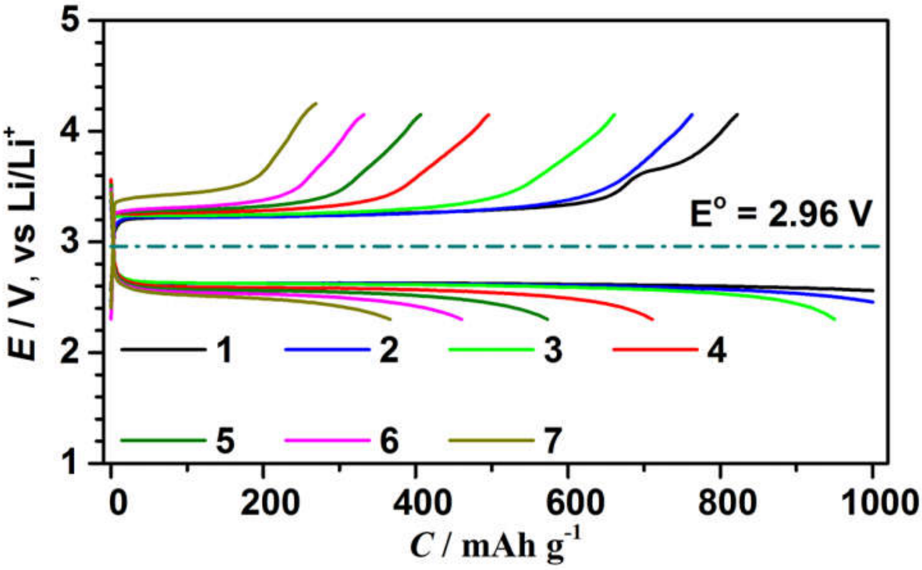

Fig. S3 The discharge-charge profiles of the initial 7 cycles of the Li-O_2 battery employing Ru/SP without EMD as cathode and the electrolyte with 4600 ppm of H_2O at 500 mA g^{-1}.

The equilibrium $Li_2O_2(s) + H_2O(l) \leftrightarrow LiOH(s) + H_2O_2(l)$ always exists at the cathode of the Li-O_2 battery with water in electrolytes. LiOH forms at cathodes as long as there is water in the electrolyte. In the charging process, the resultant LiOH can be oxidizted at ~3.2 V and regenerate H_2O to make the equilibrium move forward until the charging process is completed. But, the regeneration rate of H_2O is dependent on the equilibrium constant and the charging current, affecting the charging efficiceny.

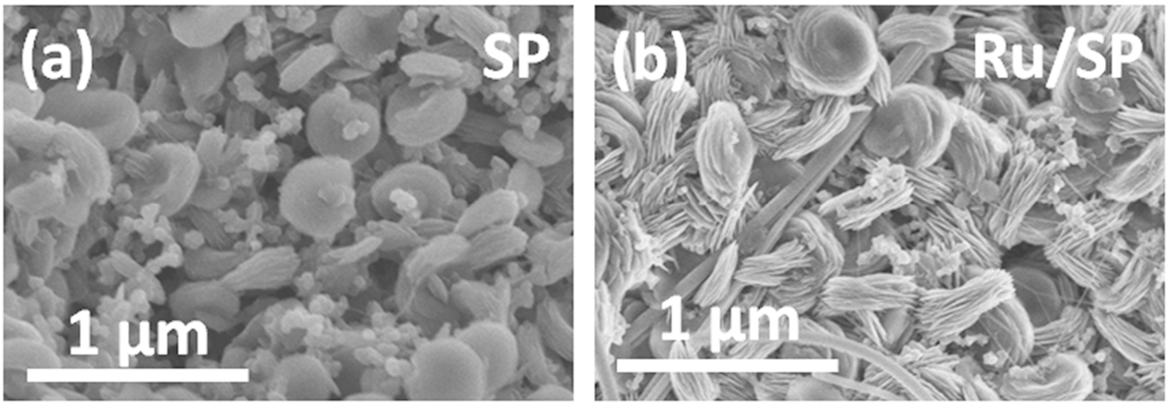

Fig. S4 SEM images of the products after the first discharge of the Li-O_2 batteries on (a) SP and (b) Ru/SP cathodes in the dry electrolyte (11 ppm H_2O), respectively.

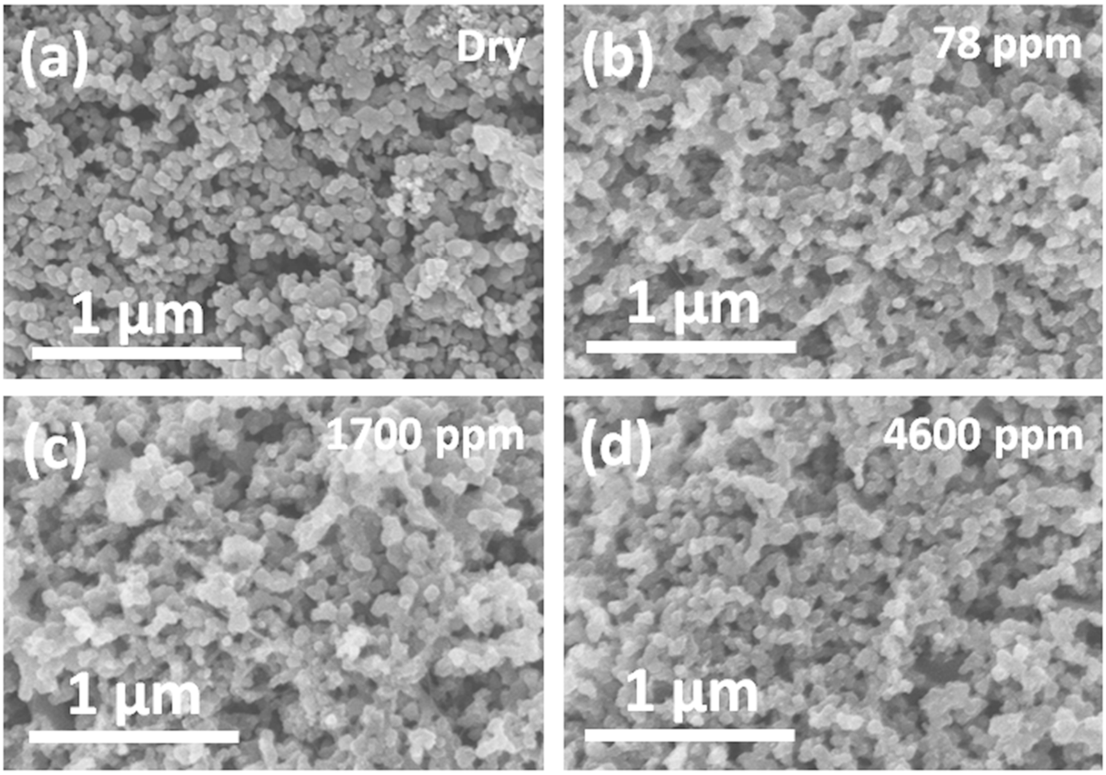

Fig. S5 SEM images of the EMD/Ru/SP cathode after charge in (a) dry electrolyte and in the electrolyte with H_2O of (b) 78 ppm, (c) 1700 ppm and (d) 4600 ppm.

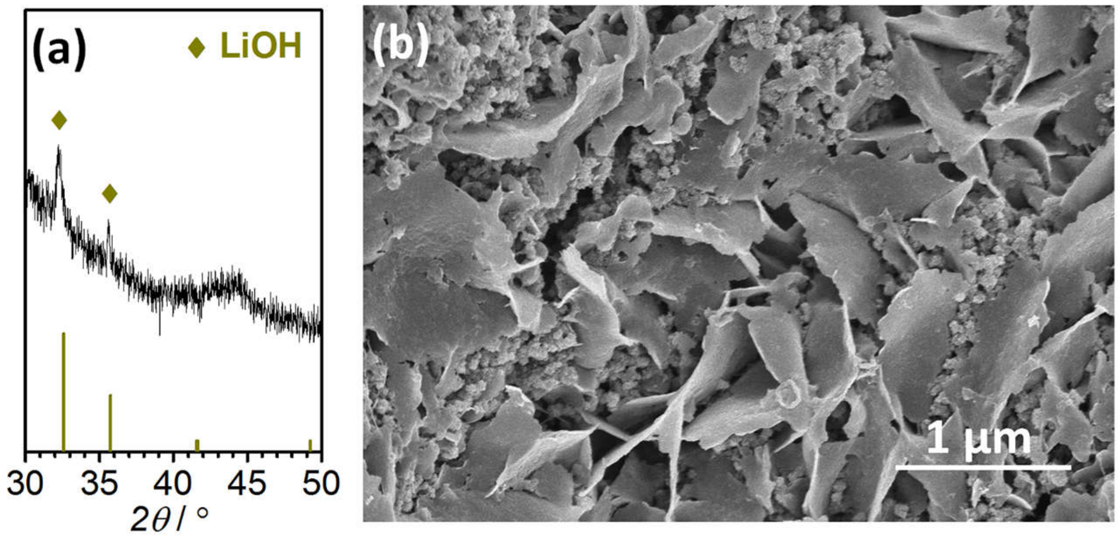

Fig. S6 (a) *Ex-situ* XRD pattern and (b) SEM image of the discharge products after 50 cycles in the Li-O_2 batteries with the EMD/Ru/SP cathode and the electrolyte containing 4600 ppm of H_2O.

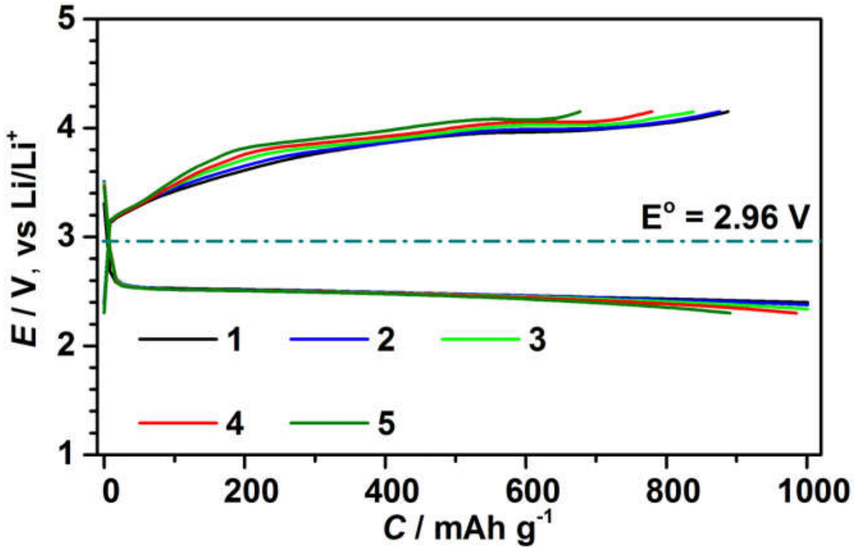

Fig. S7 The initial 5 discharge-charge profiles of Li-O_2 battery with the EMD/Ru/SP cathode and the dry electrolyte at 1000 mA g^{-1}.

Scheme S1 Proposed mechanism for the discharging and charging processes of the Li-O_2 battery with the EMD/Ru/SP cathode in the presence of H_2O in the electrolyte.

Discharging processes

Route 1

$Li^+ + O_2 + e^- \rightarrow LiO_2$ (E^0 = 3.0 V vs. Li/Li^+)[1] (1)

$LiO_2 + Li^+ + e^- \rightarrow Li_2O_2$ (E^0 = 2.96 V vs. Li/Li^+)[1] (2)

$2LiO_2 \rightarrow Li_2O_2 + O_2$ (3)

$Li_2O_2 + 2H_2O \leftrightarrow 2LiOH + H_2O_2$ (4)

Route 2

$O_2 + e^- \rightarrow O_2^{\bullet -}$ (E^0 = 3.0 V vs. Li/Li^+)[1] (5)

$O_2^{\bullet -} + H_2O + Li^+ \rightarrow HO_2^{\bullet} + LiOH$ (6)

$HO_2^{\bullet} + O_2^{\bullet -} \rightarrow HO_2^- + O_2$ (7)

$HO_2^- + H_2O + Li^+ \rightarrow H_2O_2 + LiOH$ (8)

$H_2O_2 \xrightarrow{EMD} H_2O + 1/2O_2$ (9)

Charging processes

$2LiOH \rightarrow 2Li^+ + 1/2O_2 + H_2O + 2e^-$ (E^0 = 3.32 V vs. Li/Li^+)[2] (10)

References

1 J. Lu, L. Li, J. B. Park, Y. K. Sun, F. Wu, K. Amine, *Chem. Rev.,* 2014, **114**, 5611.

2 F. Li, S Wu, D. Li, T. Zhang, P. He, A. Yamada, H. Zhou, *Nat. Commun.,* 2015, **6**, 7843.