Supporting Information

Interfacial Construction of Li_2O_2 for Performance-improved Polymer Li-O_2 Battery

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Experimental

Preparation of PMS

PMS was synthesized via emulsion polymerization as previously reported.[1] 1.5 wt% sodium dodecyl sulfate (SDS, as an emulsifier) solution was prepared with deionized water under N_2 at 60 °C. The mixture of MMA and St (with 66:34 mol ratio) was added into the SDS solution under stirring vigorously for 1 h to form emulsified solution. Sodium persulfate (as initiator) in the amount of 0.15 wt% was slowly added into the emulsified solution for the polymerization and the reaction proceeded under stirring vigorously for 7 h. The resulting emulsion was poured into 3 wt% $Al_2(SO_4)_3$ solution to yield the precipitate, which was isolated by filtration and washed with hot deionized water (50 °C) in order to remove impurities such as residual monomers and emulsifier. The copolymer P(MMA-St) in the form of white powder was finally obtained by drying the purified precipitate in a vacuum oven at 50 °C for 24 h.

Preparation of RuO_2@RGO hybrid

The RuO_2@RGO hybrid was synthesized by a mild hydrothermal reaction. [2] 18 mg GO was dispersed in 25 mL H_2O, ultrasonicated for 1 h and mixed with 30 mg of $RuCl_3 \cdot xH_2O$. After 30 min of incubation, the resulting solution was transferred to the Teflon-lined autoclave and reacted hydrothermally at 180 °C for 12 h. The precipitation was filtered, washed and dried.

Chemical stability test of PMS

The chemical stability test of PMS was performed in an argon-filled glovebox (H_2O < 0.1 ppm, O_2 < 0.1 ppm). The following describes a typical experiment. In a 15 ml vial, 20 mg of PMS was dissolved in 10 ml of THF (stored in the presence of a shining Li foil). The polymer/solvent mixture was stirred to allow the polymer to dissolve. Then 200 mg of commercial Li_2O_2 was added to allow for an excess mass concentration of Li_2O_2 as compared to the polymer mass concentration. The mixture was stirred throughout the course of the experiment.

Preparation of gel polymer electrolytes

The obtained copolymer PMS, nano-TiO_2 (Sigma-Aldrich, average particle size of 7 nm) with 10 wt% content of polymer were dispersed in THF at a concentration of 4 wt% under stirring. After complete dissolution, a commercial microporous polypropylene (PP) separator (Celgard, USA, thickness of 25 um) was immersed in the slurry for 1 h, taken out and transferred into a sink for phase inversion. The resulting membrane was washed with deionized water and immersed into deionized water for 2 h to remove THF. The porous PP/PMS/TiO_2 membrane was finally obtained after drying the membrane in vacuum at 50 ^{o}C for 24 h. In order to prepare RM@GPE, the porous membranes were immersed in an solution, 1 M lithium perchlorate ($LiClO_4$, Sigma-Aldrich, 99.95%) in tetraethylene glycol dimethyl ether (TEGDME, G4, Sigma-Aldrich, 99%), and 0.05 M LiI added as the redox mediator, in an argon-filled glovebox with water and oxygen content lower than 0.1 ppm overnight before use, while the GPE was obtained through immersing the porous membranes in 1 M $LiClO_4$/G4 solution.

Characterization

X-ray powder diffraction (XRD) patterns were recorded on a Bruker D8 X-ray diffractometer using Cu Kα (λ = 1.54 Å) radiation. The images of all the samples and electrodes were examined using scanning electronic microscope (SEM) on a JSM-6700F instrument. The discharged and recharged SEM cathodes were both washed with dimethoxyethane followed by removal of the dimethoxyethane in vacuum. The thermogravimetric analysises (TGA) were conducted on BRUKER TG-DTA 2010SA-G4H to survey thermal stability of the PP/PMS/TiO_2 membrane.

Electrochemical characterization: The electrochemical stability of GPE was investigated by linear sweep voltammogram, which were obtained on Solartron 1640 at a scanning rate of 1.0 mV s^{-1} at 25 °C in 1 atm of O_2 flow, where GPE was sandwiched between lithium anode and stainless steel (SS). The SP and RuO_2@RGO cathode were prepared by first mixing Super P (RuO_2@RGO), poly(tetrafluoroethylene) (PTFE) together with a weight ratio of 85:15, and rolled into a film, which were pressed onto carbon based gas diffusion layer (GDL 35BA, SIGRACET Gas Diddusion Media) worked as cathodes. The electrodes were dried at 100 ^{o}C in a vacuum oven for 12 h. The cells were assembled in an argon filled glovebox with water and oxygen level less than 0.1 ppm. A lithium foil was used as anode. The as-prepared GPE were sandwiched between a lithium anode and a SP (RuO_2@RGO) cathode. The cells were gastight except for the cathode side window, which exposed the cathode film to the oxygen atmosphere. Galvanostatic discharge/charge tests were conducted on the Hokuto discharge/charge system at 25 °C.

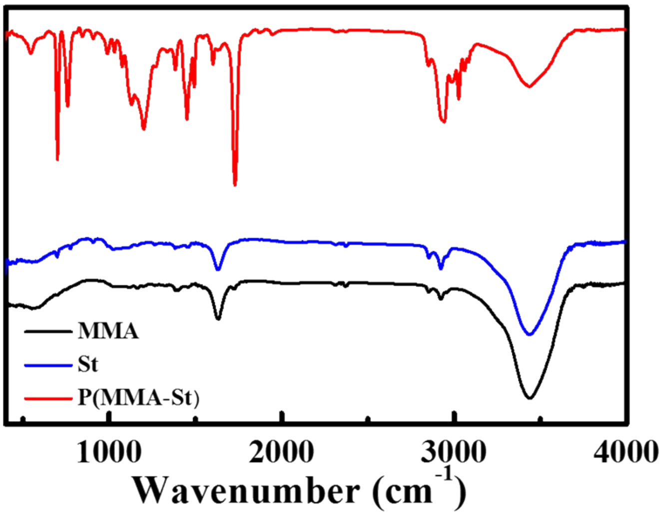

Fig. S1 FT-IR of copolymer PMS, MMA and St.

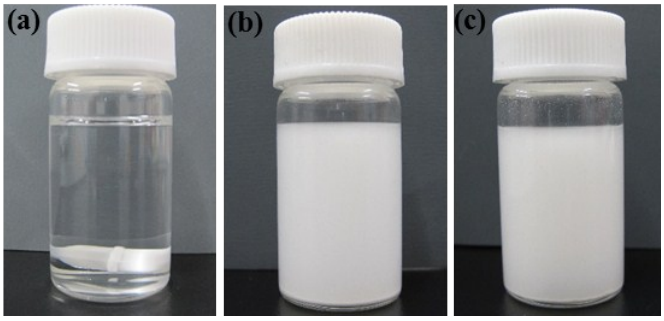

Fig. S2 Digital pictures of PMS stirred with THF (a), PMS solution with Li_2O_2 for 2 h (b) and 30 day (c), respectively.

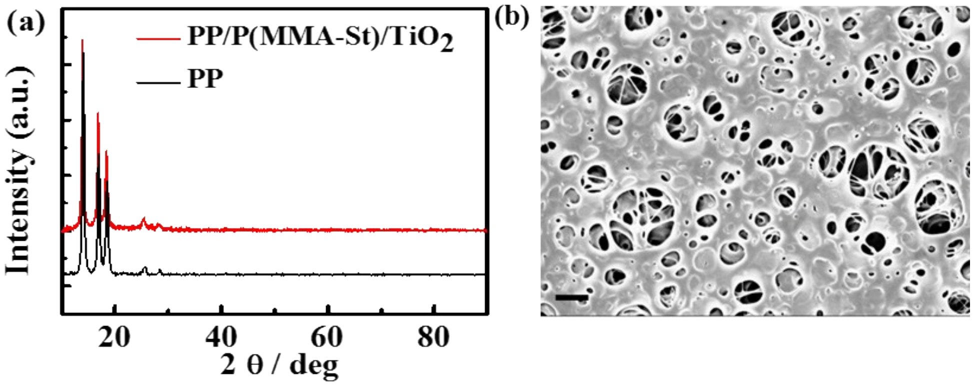

Fig. S3 (a) XRD patterns of PP/PMS/TiO_2 and PP, (b) SEM of PP/PMS/TiO_2 membrane. The scale bar is 1μm.

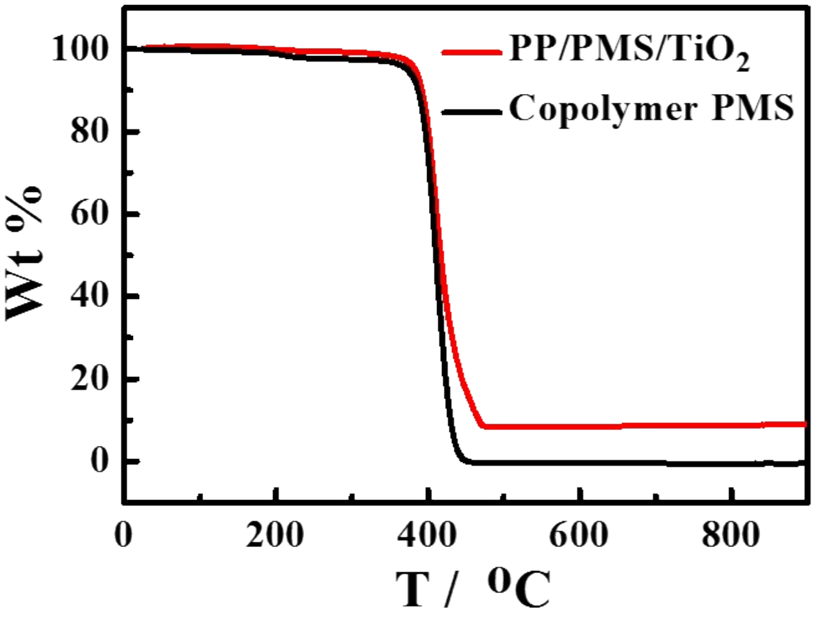

Fig. S4 TGA curves of PP/PMS/TiO_2 and copolymer PMS.

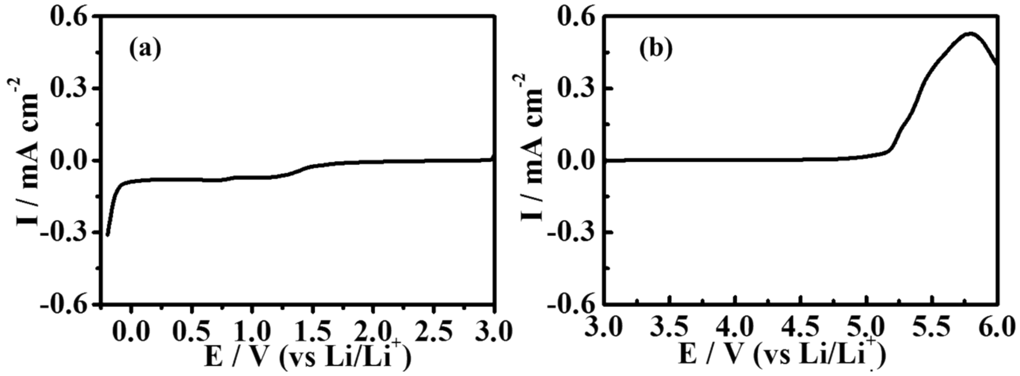

Fig. S5 Cathode (a) and anodic (b) stability of PP/PMS/TiO_2 based-GPE: scanning rate, 1 mV s^{-1}.

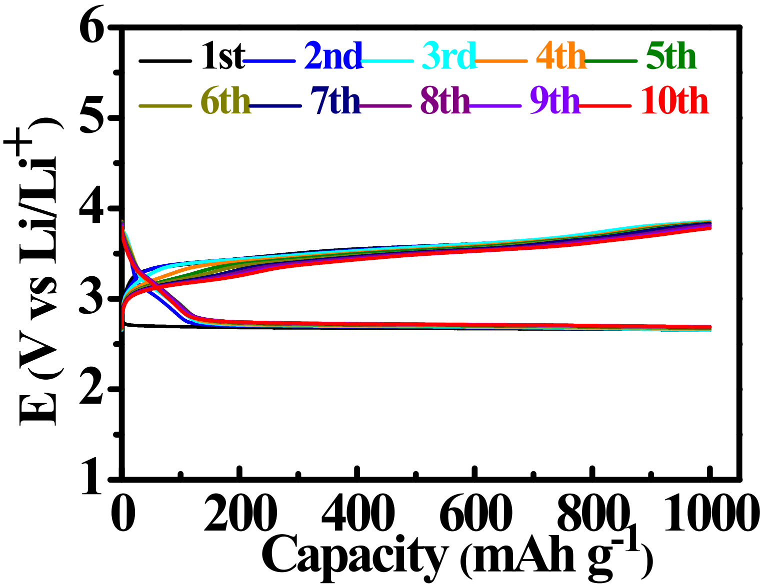

Fig. S6 Discharge/charge profiles of the first 10 cycles of the Li-O_2 battery assembled with RuO_2@RGO cathode and RM@GPE at the current density of 200 mA g^{-1} with a capacity limit of 1000 mAh g^{-1} under dry O_2.

Reference:

1 D. W. Kang, D. W. Kim, S. I. Jo and H. J. Sohn, *J. Power Sources*, 2002, **112**, 1-7.

2 H. G. Jung, Y. S. Jeong, J. B. Park, Y. K. Sun, B. Scrosati and Y. J. Lee, *ACS Nano*, 2013, **7**, 3532-3539.