Electronic supplementary information

Magnesium Ions Based Organic Secondary Battery

Experimental section

Materials: 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA, 99%) was obtained by Energy Chemical Inc. Ethylene diamine (EDA) was purchased from Aladdin. Ketjen Black (KB) and carbon black (Super P) were provided by Shanghai Xiaoyuan Energy Technology Limited. Tri-phenylamine (TPA), chloroform and anhydrous iron chloride (FeCl₃) were bought from Molbase (Shanghai) Biotechnology Co., LTD. Anhydrous magnesium perchlorate (Mg(ClO₄)₂) and anhydrous acetonitrile (AN) were purchased from Macklin (Shanghai) Biochemical Technology Co., LTD. All the reagents were analytical grade and used as received without further purification unless further mentioned. Anhydrous chloroform was distilled with CaH₂. Anhydrous Mg(ClO₄)₂ was dried under vacuum at 120 °C for 12 h before use.

Preparation of polytriphenylamine (PTPAn): PTPAn was synthesized via the literature reported procedures^{S1} by the oxypolymerization of TPA with anhydrous FeCl₃ under N_2 atmosphere. Typically, TPA (0.025 mol) was dissolved in CHCl₃ (100 mL) under stirring. Then FeCl₃ (0.1 mol) was added into the above solution in four portions with the interval of 1 h under the protection of N_2 atmosphere. Methanol (500 ml) was added to the reaction mixture after 2 h and the precipitate was then filtered and washed with methanol for 3 times. PTPAn was obtained as the off-white powder with a yield of 85.6% after the recrystallization of the filtrate with CHCl₃/acetone (containing 5% aqueous ammonia) and vacuum dried at 50 °C for 6 h.

Preparation of perylene diimide-ethylene diamine (PDI-EDA): Typically, PTCDA (0.5 mmol) and EDA (0.5 mmol) were dispersed in 1-methyl-2-pyrrolidinone (NMP, 50 mL) at room temperature by ultra-sonication. Subsequently, the mixture was thermally treated with magnetic stirring at 180 °C for 9 h to allow the condensation of PTCDA and EDA. The resulting suspension was cooled to room temperature and filtrated. The filtered solid was washed with NMP and ethanol for several times and vacuum-dried at 100 °C for 12 h to produce PDI-EDA as black powder with a yield of about 89.2%.

Structural characterization: The chemical structures of the samples were verified by the Fourier transform infrared spectra (FTIR, Nicolet 6700 spectrometer). The crystallization degree of the samples was investigated by powder X-Ray diffraction (XRD, Rigaku D/Max 2500) with Cu K α irradiation (λ =1.54 Å). The morphologies of PTPAn and PDI-EDA were characterized by scanning electron microscope (SEM, JEOL JSM-7800F Prime, 5kV) and transmission electron microscope (TEM, Tecnai G2 spirit Biotwin). X-ray photoelectron spectroscopy (XPS) measurement was performed by AXIS UltraDLD and the corresponding XPS curves were fitted with a full width at half maximum (FWHM) of 1.0-1.2.

Electrochemical measurements:

The CV profiles of PTPAn and PDI-EDA were measured in $Mg(ClO_4)_2/AN$ electrolyte (1M) in a three electrode system with a CHI760e electrochemical workstation at a scan

rate of 10 mV s⁻¹. PTPAn or PDI-EDA loaded on the graphite paper was used as the working electrode. Typically, the PTPAn electrode consisted of PTPAn powder (50 wt%), Super P(40 wt%) and polyvinylidene fluoride (PVDF, 10 wt%) and PDI-EDA electrode was composed of PDI-EDA powder (50 wt%), KB(40 wt%) and PVDF(10 wt%). The working electrodes were prepared by stirring the above mixture in NMP for 2 h to form homogeneous slurries and then spread the slurries onto the graphite paper, respectively. After vacuum dried at 100 °C for 12 h, the working electrodes were obtained. The counter electrode was prepared by mixing 70 wt% of the activated carbon (BP2000, CABOT Co. America) with 30 wt% polytetrafluoroethylene (PTFE). The reference electrode was Ag/AgCl calibrated with ferrocene/ferrocenium (Fc/Fc⁺) redox couple.

Electrochemical performances of the MIOB were tested in a CR2032 type coin cell, which comprises PTPAn as the cathode, PDI-EDA as the anode, $Mg(ClO_4)_2$ in anhydrous acetonitrile (1M) as the electrolyte and Whatman glass fiber papers as the separator. The cathodes were composed of PTPAn (50 wt%) as the active material, Super P (40 wt%) as the conductor and polyvinylidene fluoride (PVDF, 10 wt%) as the binder. And the anode consisted of PDI-EDA (50 wt%) as the active material, KB (40 wt%) as the conductor and PVDF (10 wt%). To prepare the electrodes, all the aforementioned components were mechanically mixed in NMP to form homogeneous slurries, which were spread onto graphite paper (cathode) and copper foil (anode), respectively. The obtained graphite paper and copper foil were dried under vacuum at 100 °C for 12 h and subsequently punched into discs with the diameter of 12 mm. The mass loading of the cathode and anode materials were about 0.8 and 1.0 mg cm⁻², respectively. The batteries were assembled in an argon-filled glove box with the moisture and oxygen concentrations below 1 ppm. The galvanostatic charge–discharge (GCD) tests were conducted on Land CT2001A testing system in the potential range of 0.01 to 1.6 V. The cell capacity was based on the mass of PDI-EDA in anode. The CV profiles of the samples were measured on a CHI760e electrochemical workstation at a scan rate of 0.5 mV s⁻¹.

To prepare the pouch cells, the PTPAn cathode $(3\times4 \text{ cm}^{-2})$, Celgard polyethylene separator and PDI-EDA anode $(3\times4 \text{ cm}^{-2})$ were first stacked as a sandwich-like structure and dried under vacuum at 60 °C for 6 h . And then they were put into an aluminum-lined battery pouch in an argon-filled glove box with the moisture and oxygen concentrations below 1 ppm and Mg(ClO₄)₂/AN electrolyte (1M) with rational amount was injected into the pouch. After that, the battery pouch was sealed by a vacuum heat sealing machine.

To explore the energy storage mechanism of the MIOB, the pristine MIOBs (labeled as "as-made"), the MIOBs charged to 1.6 V and discharged to 0.01 V were disassembled in the argon-filled glovebox with the moisture and oxygen concentrations below 1 ppm. And the cathode and anode were repeatedly washed with anhydrous acetonitrile for several times and then vacuum dried at 80 °C for 2h. The obtained samples were then sent for XPS and FTIR measurements.



Figure S1. Calibrating the potential of Ag/AgCl with ferrocene/ ferrocenium (Fc/Fc⁺) redox couple as internal standard and the schematic diagram of estimating Mg/Mg²⁺ voltage.



Figure S2. The cycling performances of MIOB at the current density of 1000 mA g^{-1} for 5000 cycles.



Figure S3. The full survey XPS spectra of the PTPAn cathode in different charging

state.



Figure S4. The galvanostatic discharge-charge curves of the MIOB at different temperature: a) 25 °C, b) 0 °C, c) -10 °C and d) -20 °C.



Figure S5. The galvanostatic discharge-charge curves of flexible MIOB pouch cell at different current densities.

Table S1. Electrochemical performances of the MIOB in this work and the other

Cathode	Anode	Voltage ^a	Capacity ^b / Current density	Cycles/ Capacity ^b / Current density	High rate capacity ^b	Ref.
+0~0 \$0*	 }\$\$\$\${~},	1.1	90/50 mA g ⁻¹	1000/73/ 1000 mA g-1	73/ 1000 mA g ⁻ 1	This work
Mo ₆ S ₈	Sn	0.85	82/-	10/45/-	-	S2
PBN	polyimide	0.85	36/0.2 A g ⁻¹	5000/22/ 2 A g ⁻¹	15/10 A g ⁻¹	S3
V ₂ O ₅	Sn	0.65	100/0.04 A g ⁻	50/120/ 0.04 A g ⁻¹	-	S4

magnesium ion batteries.

Mg-OMS-2	Activated	1.0	46/0.1 A g ⁻¹	500/44.1/		85
	Carbon			0.1 A g ⁻¹	-	
MgCoSiO ₄	Activated	1.0	73.0 /0.02C	30/88/		S6
	Carbon			0.02 C	-	
KNF-086	Activated	0.41	48.3/0.2C	30/33/	11 5/4 C	S7
	Carbon			0.2 C	11.5/4 C	

^a Average discharge voltage, V.

^b Discharge specific capacity, mA h g⁻¹.

Reference

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