

1. Experimental section

1.1 MgO decomposition test

The reaction of iodine with MgO was investigated at 60° C. In a 9 mL glass tube, 650 μmol of MgO (purity 99.999%, Aldrich) was suspended in 3 mL of iodine solutions of various concentrations. The amount of iodine varied between 3.75 and 7.54 μmol. The solvents used were dimethyl sulfoxide (DMSO, NMR grade), acetonitrile (AN, Super Dehydrated grade), dimethylformamide (DMF, Super Dehydrated grade), and toluene (TOL, Super Dehydrated grade). The four organic solvents used were available from Wako Chemicals.

Tri-*t*-butyl phosphate (TBP, 99%, Aldrich) was also tested. The glass tubes were heated at 60° C for 96 hours. Quantitative analysis of Mg in the iodine solutions was carried out after heating by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Gas chromatography-mass spectrometry (GC/MS) was carried out on a GC/MS spectrometer (Agilent Technologies, GSLG9810) to investigate gas composition after the heating of the DMSO sample. The constant flow rate of argon was 7 ml/min.

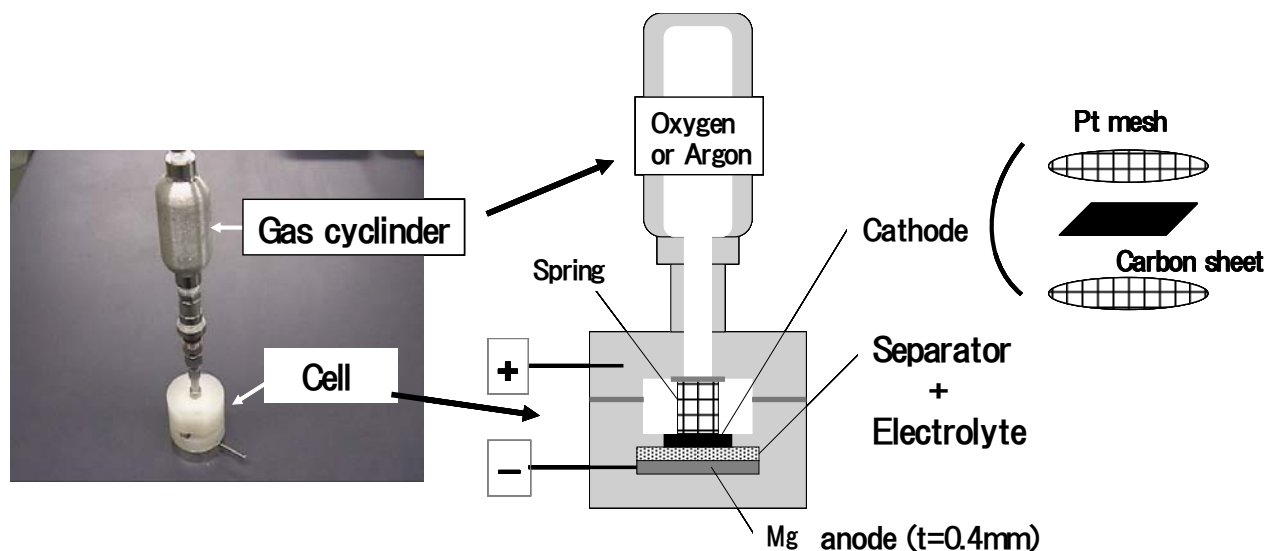
1.2 Catalytic mechanism

Carbon sheets were prepared by dry mixing of Ketjen black (Mitsubishi Chemicals, ECP-600JP, 85% by weight) with Teflon powder as a binder (Daikin, F-104, 15%). The carbon electrode containing MgO was formed by dry mixing of Ketjen black (47% by weight), MgO (38%) and Teflon powder (Daikin) as a binder (15%). The carbon electrode containing MgI₂ (Aldrich) was formed by dry mixing of Ketjen black (46% by weight), 41% MgI₂ and 13% Teflon powder as a binder. Electrochemical cells with the carbon cathode, Mg anode, and an electrolyte solution containing iodine were fabricated using a modified F-type cell (Hokuto Denko Corp. SI Fig.3) under argon. The carbon sheet (weight 4 mg, area 0.64 cm², thickness 0.16 mm) prepared by dry mixing was sandwiched with two 80-mesh Pt grids (Nilako) as the cathode.

Three 25 μm-thick polyethylene sheets (Tonon Chemical Corp.) were used as separators. The electrolyte contained 0.5 mol/L magnesium perchlorate (Aldrich) as a supporting salt dissolved in DMSO (Kishida Chemical, battery grade). The concentration of iodine in the solutions was 0.026 mol/L. We poured 0.3 mL of the electrolyte into the cell. The electrical capacity of the iodine in the electrolyte (0.3 mL) was 0.42 mAh. The cell operated under argon. The charging test was started with a Hokuto Denko potentiometer (HJ1001SM8A) using a current density of 0.078 mA/cm². Cyclic voltammograms of 0.25 mol/L Mg(ClO₄)₂-DMSO solutions free of iodine were recorded at 60° C using a potentiometer (Ivium). The working and counter electrodes were Pt, the reference electrode was Ag⁺/Ag, and the scanning rate was 10 mV/sec.

1.3 Electrochemical tests

Electrochemical cells were fabricated with the carbon cathode sandwiched between two Pt mesh grids, an Mg anode, and an electrolyte solution containing iodine under argon, and setting an oxygen bomb at 2 atm as the cathode (ESI Fig.1). Three polyethylene separator sheets were used as above. The electrolyte was a 0.5 mol/L Mg(ClO₄)₂ solution in DMSO. The concentration of iodine in the solutions was between 0.026 and 0.086 mol/L, and 0.3 mL of the electrolyte solution was poured into the cell. The electrical capacity of iodine in the electrolyte (0.3 mL) was 0.42 mAh. The discharging-charging behavior of the air cells was measured with an Asaka Charge/Discharge system (ACD-MO2) using a 0.05 mA (0.078 mA/cm²-cathode) discharge current at 60° C. When the discharge voltage reached 0.7 V, the current was reversed. The charging was continued up to a voltage of 2.8 V with a current of 0.03 mA (0.047 mA/cm²) at 60° C.

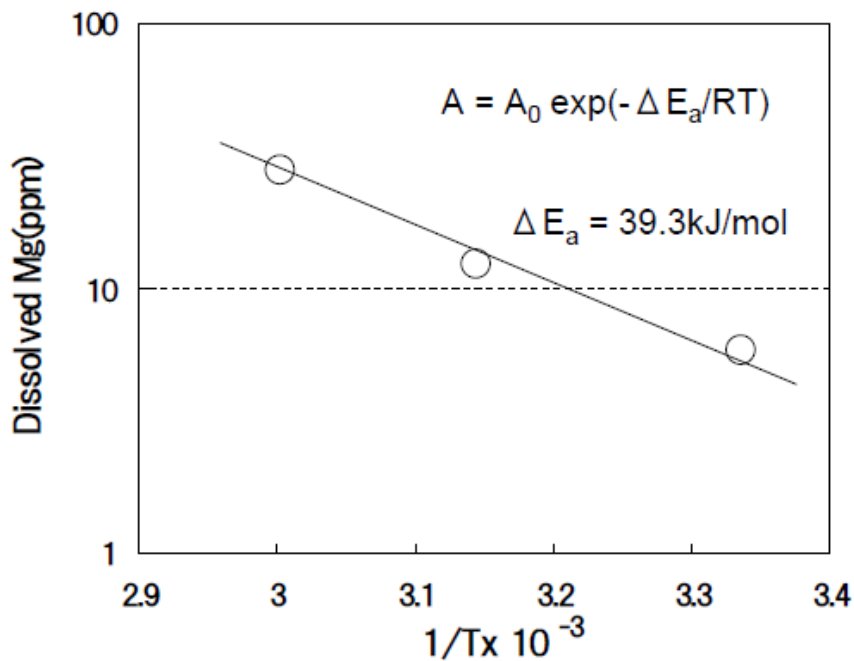


ESI Fig.1 A schematic illustration of the modified F-typed Cell

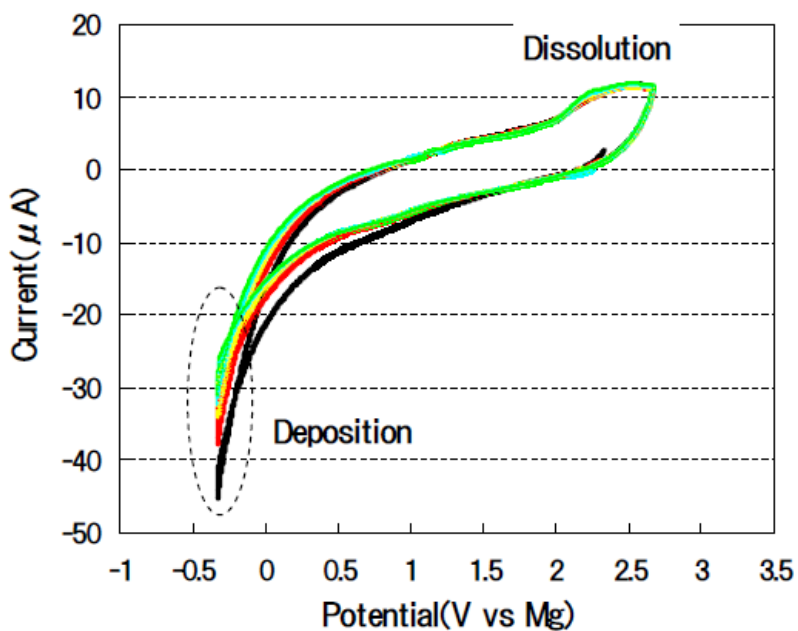
1.4 Surface analyses

Raman spectroscopy was carried out in a JASCO laser Raman spectrophotometer (NRS 3300) to study the discharge reaction. The wavelength of the excitation laser was 532 nm. The spot of laser excitation was 30 μ m in diameter. TOF-SIMS measurements were performed using a TOF-SIMS spectrometer (ION-TOF GmbH, TOFSIMS-5). The area of the SIMS analysis was 0.5 mm \times 0.5 mm.

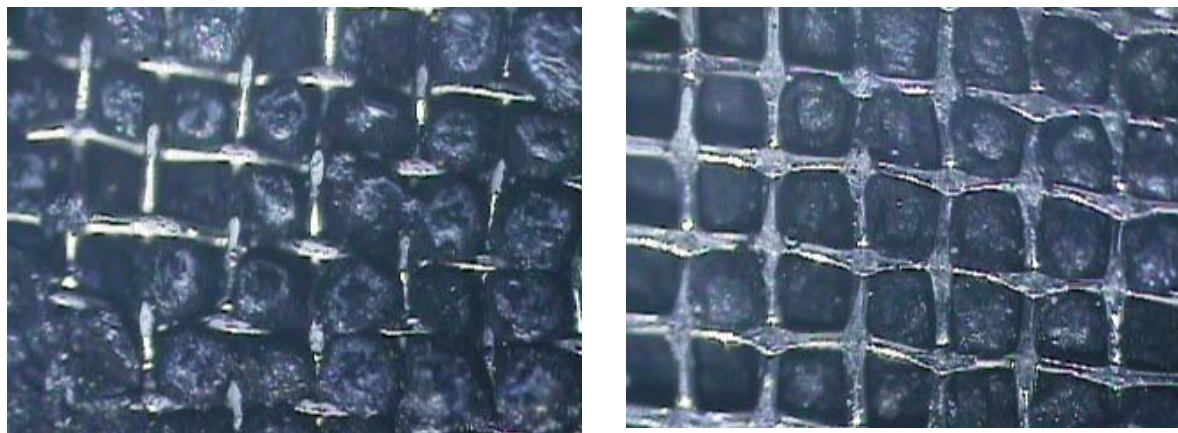
2. Experimental Data



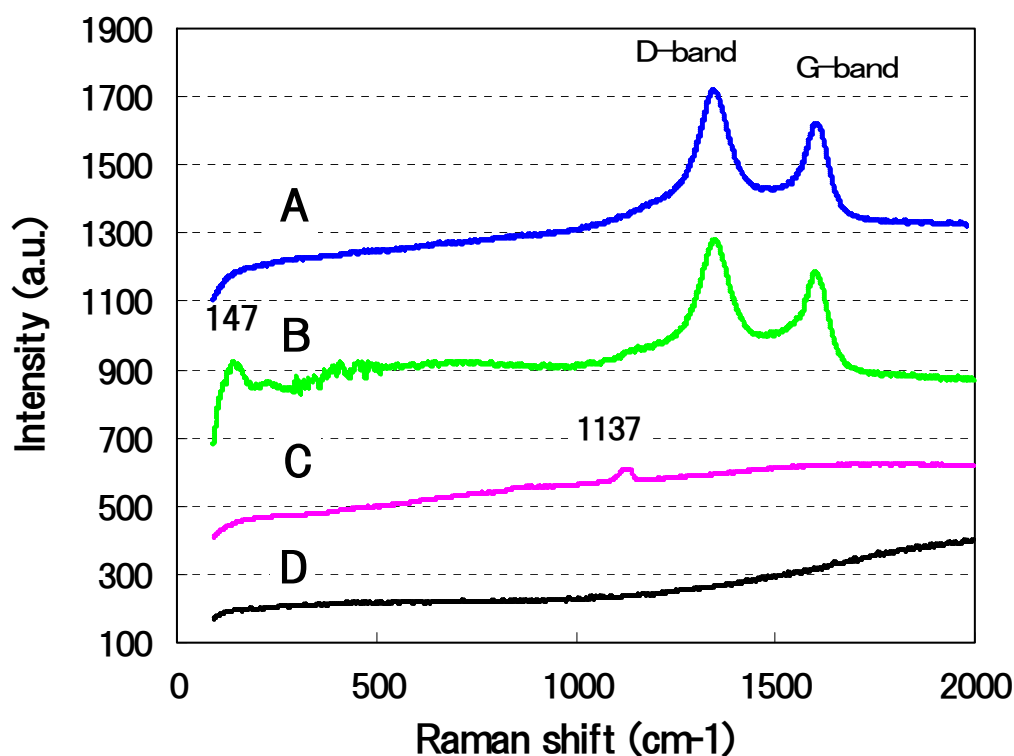
ESI Fig.2 Decomposition of MgO by I_2 -DMSO complex at ambient temperatures



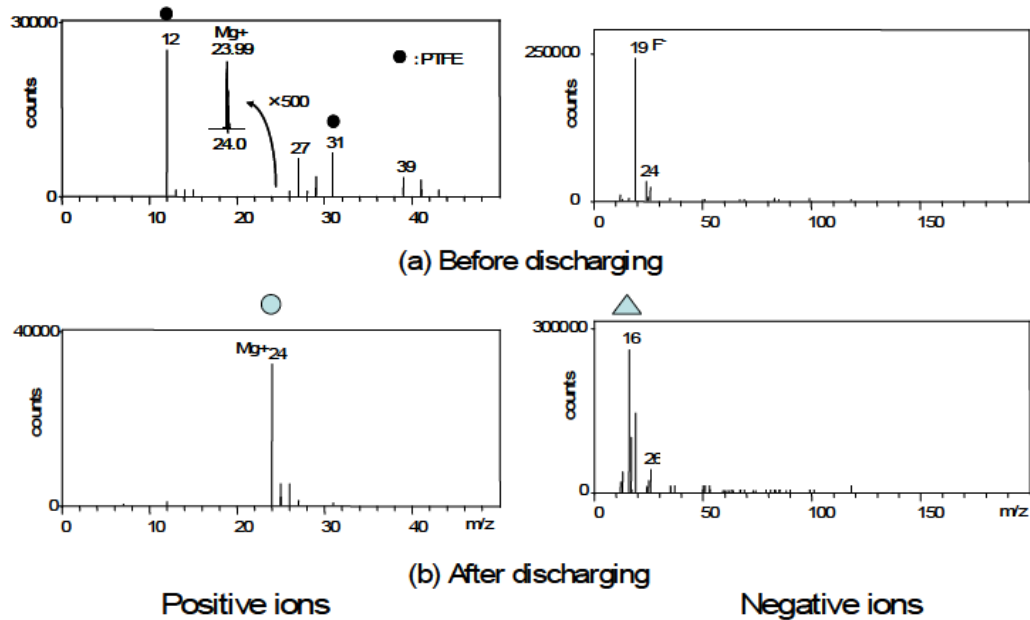
ESI Fig.3 CV profiles of $Mg(ClO_4)_2$ -DMSO solution (1st – 5th cycles)



ESI Fig.4 Photographs of the precipitates at cathode of Mg-O₂ battery using I₂-DMSO complex, (left) after only discharging of 2439 mAh/g, and (right) after discharging of 2131mAh/g and charging of 1801mAh/g. The separation between mesh wires was 0.25mm.



ESI Fig.5 Raman spectra of the precipitates at cathode after discharging/charging (A) and after only discharging (B), reagents of MgO₂ (C) and MgO (D).



ESI Fig.6 TOF-SIMS spectra of the cathodes (a) before and (b) after discharging. The symbols of O and Δ represent the signals at $m/Z=24$, and at $m/Z=16$, respectively.

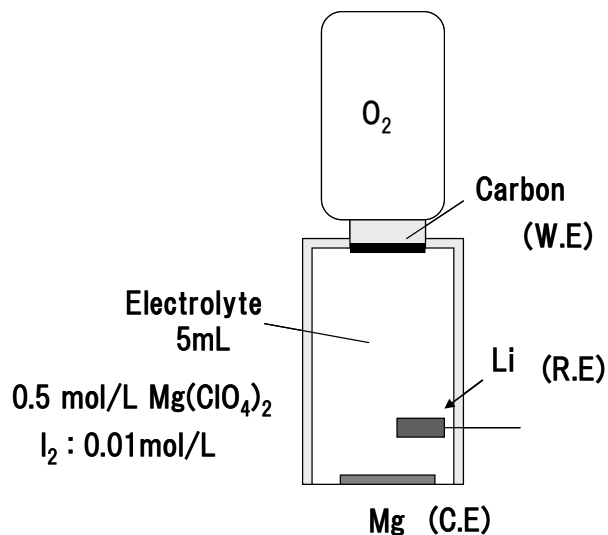
Table I Gases generated in the charging test

Sample	O ₂	H ₂	CO	CO ₂	CH ₄
Cell A	0.00	0.10	0.00	0.03	0.00
Cell B	0.00	0.22	0.00	0.21	0.02
Cell C	1.57	0.67	0.00	0.76	0.07

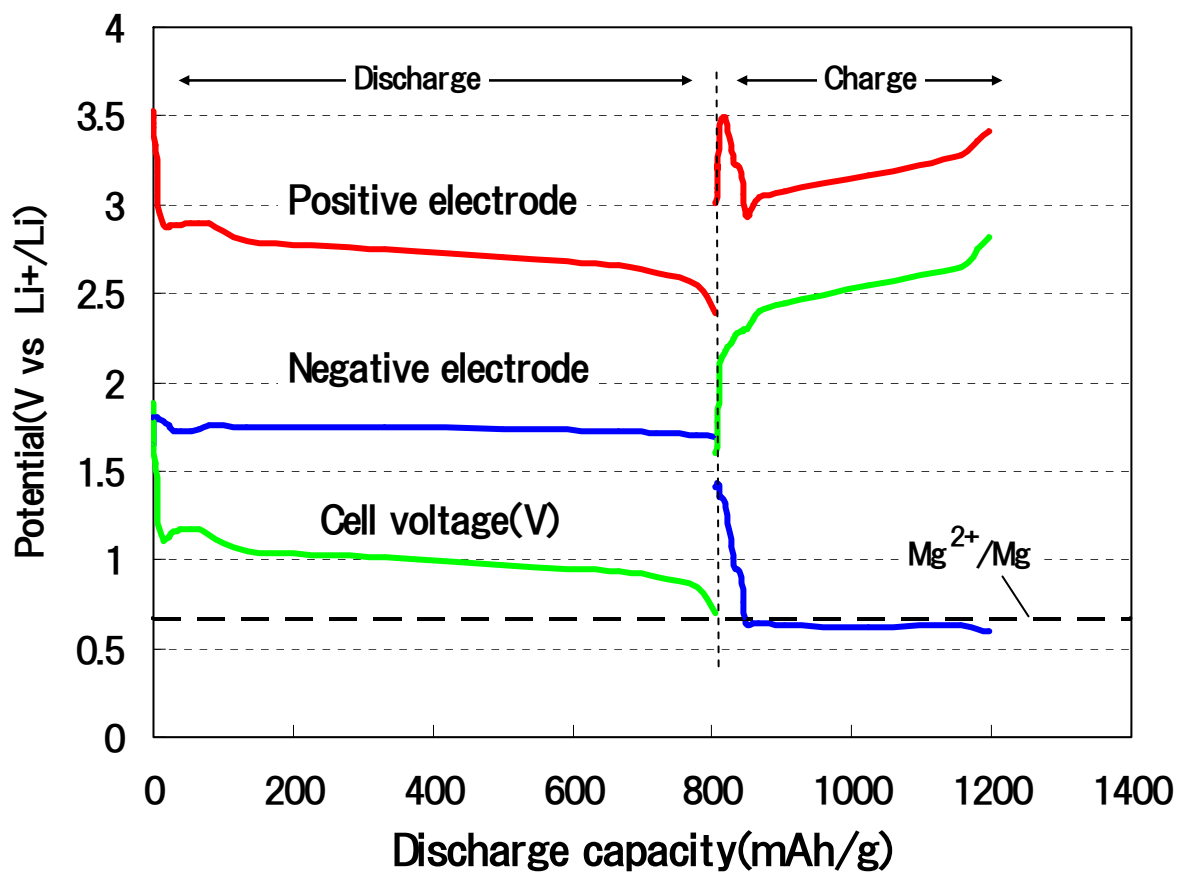
(unit: cc)

The potential profiles of the positive and negative electrodes in our Mg-O₂ cells were measured by using a three-electrode test cell. The schematic illustration of the test cell was shown in ESI Fig.7. Lithium was used as a reference electrode. The weight of the cathode material was 3.2mg. The concentration of iodine in the electrolyte was 0.01mol/L. The discharge started under a current of 0.075mA. The charge current was 0.025mA.

The cell worked voltages between 0.6V and 2.9V. ESI Fig.8 shows the potential profiles and the cell voltage in the discharging / charging. The discharge and charge curves of the cell (green line) reflected mainly on the change in the potential of the positive electrode (red line). The negative electrode (blue line) showed a potential near 1.7V during discharging. It was found that the SEI between Mg anode and the electrolyte influenced the potential for dissolution of Mg at the anode ($\text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}^-$). On charging, the potential of the negative electrode has reached 0.67V vs. Li⁺/Li, indicating that the deposition of Mg occurred at the anode in our Mg-O₂ battery.



ESI Fig.7 A schematic illustration of three-electrode Test cell



ESI Fig. 8 the potential profiles of the positive and negative electrode, and cell voltage