



Research Report

Catalytic Cycle Employing a Redox-mediator to Obtain a Secondary Mg-O₂ Battery

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■ABSTRACT■ Non-aqueous Mg-O₂ batteries are suitable only as primary cells, because MgO precipitates formed during discharge are not decomposed electrochemically at ambient temperatures. Therefore, we have examined the catalytic activity of an iodine-dimethyl sulfoxide (DMSO) complex and the 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-anion complex to catalyze the decomposition of MgO. It was determined that these complexes are capable of chemically decomposing MgO at 60°C. A catalytic cycle for the realization of a rechargeable Mg-O₂ electrode was designed by combining the decomposition of MgO via these mediators and their redox-couples. This is the first demonstration of a non-aqueous Mg-O₂ battery that incorporates an iodine-DMSO electrolyte and shows evidence of being rechargeable. In addition, we report that a Mg-O₂ battery with an acrylate polymer having TEMPO side units in the cathode is capable of several discharge/charge cycles.

■KEYWORDS■ Secondary Mg-O₂ Battery, Catalytic Cycle, Redox-mediators, Iodine-solvent Complex, TEMPO-anion Complex

1. Introduction

Battery devices with high specific energy density that are also safe to operate are currently in demand for plug-in hybrid vehicles (PHEV) and fully electric vehicles (EV), which promise effective fuel consumption and a reduction in greenhouse gas emissions. Conventional Li-ion batteries (LiBs), which operate based upon Li-ion intercalation/deintercalation at the cathode and anode, have been employed for PHEV and EVs to date. Although these LiBs have volumetric energy densities of 800 Wh/L at most, it is generally accepted that other energy storage processes can be designed to overcome 1000 Wh/L. Non-aqueous metal-air batteries are distinct candidates for expected volumetric energy densities higher than 1000 Wh/L. Especially, non-aqueous Li-O₂ battery has received much attention over the last decade.⁽¹⁻⁴⁾

The Li-O₂ batteries utilize the deposition and dissolution of lithium at the anode, and the reaction between Li ions and oxygen molecules, ideally from air, at the cathode. One of the problems with the Li-O₂ battery is that a large amount of lithium peroxide (Li₂O₂) is precipitated at the cathode during discharging.⁽⁵⁻⁷⁾ Li₂O₂ is a hazardous, explosive chemical and it therefore poses a challenge to safely incorporate this battery into vehicles. The Mg-O₂

battery also has the potential to deliver energy levels of 1000 Wh/L. In this device, Mg²⁺ interacts with oxygen species via reaction in an organic solvent ($2\text{Mg}^{2+} + \text{O}_2 + 4\text{e}^- \rightarrow 2\text{MgO}$), such that magnesium oxide (MgO) is formed at the O₂ electrode during discharge. MgO is both thermodynamically and electrochemically stable; therefore, this battery is expected to be much less hazardous. However, MgO formed at the O₂ electrode cannot be decomposed by charging at ambient temperatures.^(8,9) Therefore, although non-aqueous Mg-O₂ batteries may operate as primary cells, a charging catalyst that accelerates the decomposition of MgO would be required to allow their use as secondary cells.

A redox couple is defined as being able to assume both the oxidized and reduced forms and take part in both oxidation and reduction half-reactions. The transfer of electron occurs electrochemically between a reducing species A and its corresponding oxidized form B. In some redox couples, the oxidant B has the capability of reaction with alcohol, i.e. as a catalyst. If the oxidant B reacts chemically with magnesium oxide MgO (which B changes into A) and returns electrochemically to the initial state B, then a catalytic cycle can be constructed using the redox couple to repeatedly decompose MgO. Thus, following a search of redox couples for the decomposition of MgO, we report on two redox couples that can react with MgO, iodine,

and 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) in this paper. The former redox couple of $I_2/2I^-$ shows a potential of 3.5 V versus Li^+/Li . Iodine dissolves in some organic solvents and is complexed with the solvent molecules. We have determined that the iodine-dimethyl sulfoxide (DMSO) complex is capable of effectively decomposing MgO. TEMPO is a stable radical species and is well known cathode material for radical based batteries. However, the TEMPO-anion complex can also be used as a charging catalyst for the decomposition of MgO. We have designed a charging catalytic cycle using these redox-mediators to decompose MgO formed at the cathode (Mg-O₂ electrode) and evaluate the charge/recharge cycles of these Mg-O₂ batteries.

2. Concept of Charging Catalytic Cycle

In our previous paper,⁽¹⁰⁾ we reported on the TEMPO-anion complex ($TEMPO^+X^-$) as a charging catalyst for a non-aqueous Li-O₂ battery. The catalytic mechanism is as follows. Firstly, the complex of TEMPO with an anion occurs upon charging. The TEMPO-anion complex ($TEMPO^+X^-$, oxidized form) then reacts with Li₂O₂ aggressively and transforms into pristine TEMPO (reductant). Finally, the TEMPO unit returns to the $TEMPO^+X^-$ complex via association with the anion during charging. The catalytic cycle is constructed by the combination of Li₂O₂ decomposition with the TEMPO redox couple, which acts as a mediator.

In the same manner, we have designed a catalytic cycle for the decomposition of MgO (discharge product at the cathode of the Mg-O₂ battery). Consider a redox couple that goes back and forth between A-state (reductant) and B-state (oxidized form) (Fig. 1). When charging is started, the A-state changes electrochemically into the B-state. The B-state then

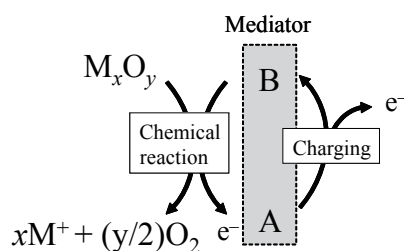


Fig. 1 Model for the catalytic cycle employing a redox-mediator to obtain a secondary Mg-O₂ battery.

acts as a catalyst to chemically decompose metallic oxides M_xO_y and return to the original state (A-state). The A-state changes to the B-state again during charging. MgO decomposition and the change of A into B by charging occurs repeatedly until M_xO_y disappears at the cathode. Therefore, to achieve a rechargeable Mg-O₂ electrode requires a redox-mediator that has the capability to chemically decompose MgO.

3. Results and Discussion

3.1 Iodine Mediator

It is known that complexation may occur between iodine molecules and certain organic solvents, including alkylamines, organophosphorus esters and phosphine sulfides.^(11,12) The formation of such complexes, consisting of a single I₂ molecule and a single solvent molecule, occurs as the result of a charge-transfer interaction between the iodine σ bond, serving as the acceptor, and the solvent's functional group, which acts as the donor.⁽¹³⁾ In previous work, we found that complexes consisting of iodine with either DMSO or trimethyl phosphate undergo an uncharacteristic reduction near 4 V vs. Li^+/Li , in contrast to the one-electron or two-electron reduction reactions of iodine species in non-aqueous solvents that proceed at values less than approximately 3.5 V vs. Li^+/Li .^(14,15) Bsiley et al. assessed catalysis by halogen-solvent complexes and determined that the oxidation of alcohols is promoted by a bromine-DMSO complex.⁽¹⁶⁾ Based on this result, it is possible that iodine-solvent complexes may also be catalytic, so the present work assessed the catalysis of MgO decomposition by various iodine-solvent complexes.

In these trials, the Mg ion concentrations in solution were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) after heating dispersions of MgO particles in various iodine-solvent solutions at 60°C. These trials determined that the Mg concentrations in the heated solutions were on the order of 10 ppm, and that the Mg concentration was raised as the amount of iodine in the solution increased. A Mg concentration of 3.70 μ mol was obtained at an iodine level of 3.77 μ mol, showing that 0.56% of the suspended MgO (655 μ mol) had been decomposed in I₂-DMSO solution. The ratio of the Mg and iodine concentrations found here is close to the 1:1 ratio that would be expected if all the Mg in

solution had been generated by MgO decomposition. It should be noted that these Mg ions could not have come from Mg present as an impurity in the original MgO, since it had a purity of 99.999%. In addition, in trials in which the solutions were instead maintained at 25°C, a lower Mg concentration of 5.8 ppm was determined.

The resulting Mg concentrations are shown as functions of literature values of the complex-formation energy, $-\Delta H$, in **Fig. 2**. It is evident from these data that iodine oxidation occurred more readily following complex formation, since the Mg concentrations are seen to increase with increasing values of the $-\Delta H$. The results of these trials demonstrated that higher temperatures increase the decomposition reaction rate and allowed us to calculate the associated activation energy of 39.3 kJ/mol.

Scheme 1 shows the more likely of the two possible MgO decomposition mechanisms, while an alternate process involving two-step decomposition via the generation of hydroiodic acid (HI) is presented in Scheme 2:

Scheme 1:



Scheme 2:

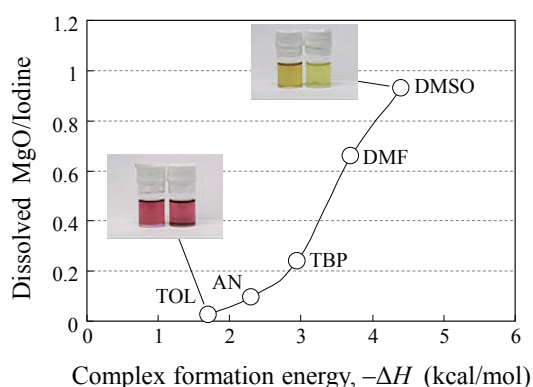
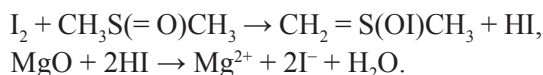


Fig. 2 Relationship between the molar-ratio of dissolved MgO to added iodine, and the complex-formation energy, $-\Delta H$. The inset photographs show the toluene (TOL) and dimethyl sulfoxide (DMSO) solutions without (left) and with (right) MgO particles after the heating test. The solvents used were toluene (TOL), acetonitrile (AN), tri-*n*-butyl phosphate (TBP), dimethyl formamide (DMF), and dimethyl sulfoxide (DMSO).

The reaction shown in Scheme 1 generates oxygen and involves the reaction of one mole of iodine with one mole of MgO. The validity of this scheme was investigated by heating a combination of 650 μmol MgO and 150 μmol iodine in DMSO and quantifying the resulting gases, including oxygen, using gas chromatography-mass spectrometry (GC/MS), with the results summarized in **Table 1**. The product gases shown here, other than oxygen, resulted from combustion of carbon in the cathode or solvent decomposition. The 1.24 mL oxygen generated by the decomposition reaction was sufficiently close to the value of 75 μmol (1.67 mL) that was calculated from the stoichiometric relationship in Scheme 1 and the reagent quantities applied, assuming complete reaction of the iodine. Based on this result, Scheme 1 is believed to represent the primary reaction pathway in an I_2 -DMSO solution.

The decomposition of MgO, catalyzed by the I_2 -DMSO complex, can be combined with the I_3^-/I^- redox couple to suggest a catalytic cycle responsible for charging at the Mg- O_2 electrode. The initial discharge step consists of precipitation of magnesium iodide (MgI_2) at the cathode, followed by depositing of the primary air battery reaction product, magnesium oxide (**Fig. 3**). **Figure 4** shows the initial charging process, during which the MgI_2 generated during the cathode discharge is reduced to generate iodine via an electrochemical process. This iodine subsequently forms a molecular complex with the DMSO that reacts

Table 1 Gases generated by heating the MgO-iodine-DMSO solution.

Gas	O_2	H_2	CO_2	CH_4
Experimental	1.24	0.08	0.43	0.06
Theoretical	1.67	0.00	0.00	0.00

(unit: mL)

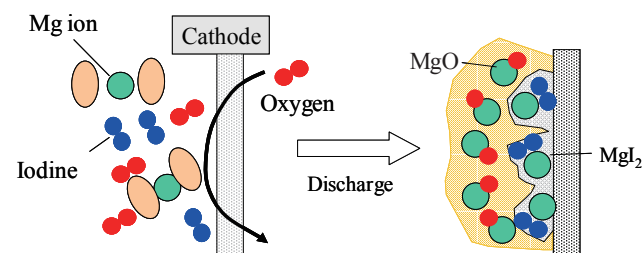


Fig. 3 Formation of MgI_2 and MgO at the cathode during discharge.

with the MgO produced through discharge at the cathode. In the last step, the precipitated MgO breaks down into Mg ions (present as MgI_2) and oxygen. Because the $3\text{I}^-/\text{I}_3^-$ redox potential vs. Mg^{2+}/Mg is in the vicinity of 2.0 V, the above process repeats until, theoretically, all the MgO is depleted from the cathode, at approximately 2.0 V.

The discharge/charge curves obtained from a Mg- O_2 battery at 60°C both with and without iodine are presented in Fig. 5,^(17,18) in which a plateau at approximately 1.2 V and a discharge capacity of 2250 mAh/g are evident in the case of the device without iodine (blue line). This battery, however, appears to function as a primary cell since it exhibits an insufficient charging capacity. In contrast, the

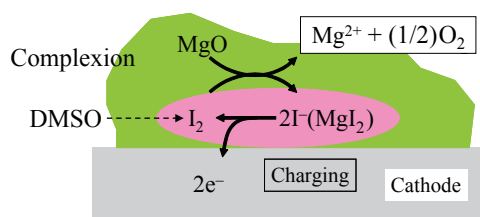


Fig. 4 Schematic illustration of the charging mechanism with the iodine-mediator.

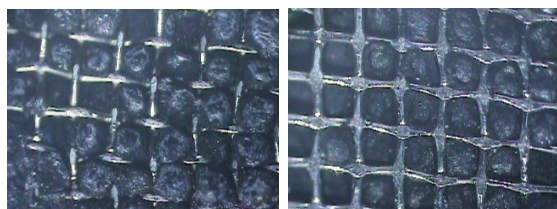
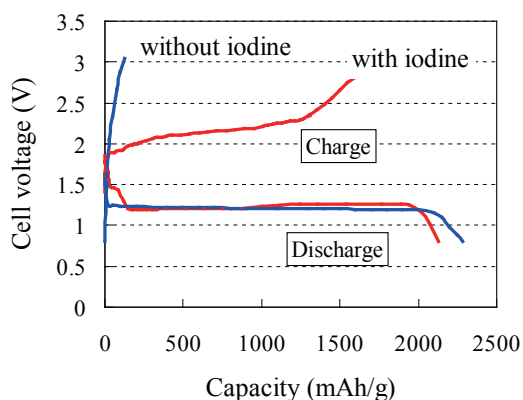


Fig. 5 Discharge/charge curves for Mg- O_2 batteries with an iodine-DMSO electrolyte at 60°C . Micrographs show the cathodes after discharge (left) and charge (right). The separation between meshes was 0.25 mm.

device in which iodine is present in the electrolyte generates two cell voltage steps throughout the first discharge, the first of which (near 1.5 V) results from the reaction of Mg^{2+} with iodine such that I_3^- is reduced ($\text{I}_3^- + 2\text{e}^- \rightarrow 3\text{I}^-$), during which the device functions as a Mg-iodine battery. This battery shows a discharge capacity of 100 mAh/g, resulting from the presence of dissolved iodine in the electrolyte. The subsequent step at approximately 1.25 V corresponds to a Mg- O_2 battery discharge, to give an overall discharge capacity of 2131 mAh/g-cathode (red line). The Mg-iodine and Mg-air batteries generated discharge voltages below the values predicted based on theoretical consideration of the iodine redox couple (+0.4 V vs. NHE) or the four-electron oxygen reduction (0.2 V vs. NHE) and Mg^{2+}/Mg (-2.37 V vs. NHE) potentials. The generation of a solid electrolyte interface (SEI) on the Mg anode is believed to have led to this lower than expected voltage. Reversing the current polarity during charging increased the cell voltage to approximately 1.8 V and also produced a plateau at approximately 2.2 V, together with a total charge capacity of 1590 mAh/g and 74.6% reversibility against discharging.

The micrographs in Fig. 5 show the cathodes after discharge and after charge. The white precipitates were identified to be MgO from Raman spectroscopy and time-of-flight-secondary ion mass spectrometry (TOF-SIMS) measurements. The white precipitates shown in the micrographs diminished during the charging process. The gases detected during the charging process were 1.92 mL of O_2 , 0.32 mL of CO_2 , 0.86 mL of H_2 , and 0.06 mL of CH_4 . The latter three gasses were generated at the anode and indicate the decomposition of DMSO molecules. Therefore, it was concluded that the battery with iodine worked as a rechargeable cell.

3.2 TEMPO-anion Complex Mediator

The acrylate polymers with TEMPO as a side pendant are the so-called radical polymers (PTMA). The TEMPO unit exhibits a redox couple with an anion X^- near 3.5 V vs. Li^+/Li (Eq. (1))⁽¹⁹⁻²⁰⁾ as follows:



We have previously reported⁽²⁰⁾ that Li_2O_2 , the discharge product in the Li- O_2 battery, is immediately decomposed by the TEMPO-anion complex

(TEMPO⁺X⁻). We have proposed a catalytic cycle using TEMPO⁺X⁻ for the charging of Li-O₂ battery (Fig.1, M_xO_y = Li₂O₂). The target of the present study was MgO instead of Li₂O₂. The TEMPO-anion complex decomposes MgO chemically, so that a charging catalytic cycle can be designed in the same manner to realize a rechargeable Mg-O₂ battery. Therefore, the ability of the TEMPO-anion complex to catalyze the decomposition of MgO was tested.

The reaction of TEMPO⁺ClO₄⁻ with MgO was investigated at 60°C. 556 μmol of MgO (purity 99.999%, Aldrich) was suspended in a solution of TEMPO⁺ClO₄⁻ (49.6 μmol) and acetonitrile (3 mL) in a 9 mL glass tube. The glass tube was heated at 60°C for 96 h. Quantitative analysis of Mg in the iodine solution was then conducted after using ICP-AES. It was confirmed that after heating, Mg ions are present in the solution at a concentration in the order of 10 ppm. When the amount of TEMPO⁺ClO₄⁻ added was 49.6 μmol, the amount of dissolved Mg in the solution was 7.98 μmol, which corresponds to 1.43% of suspended MgO (556 μmol). If all of the dissolved Mg had originated from the decomposition of MgO, then the ratio of MgO to TEMPO⁺ClO₄⁻ would be 0.16. For heating at 25°C, the concentration of dissolved Mg was 2.2 ppm. The reaction was promoted by higher temperatures and the activation energy calculated from the Arrhenius equation was 76.6 kJ/mol.

Figure 6 shows the discharge-charge profiles for the Mg-O₂ battery with PTMA in the cathode at 60°C, when the discharge capacity of the first cycle was 737 mAh/g.⁽²¹⁾ When the polarity of the current was

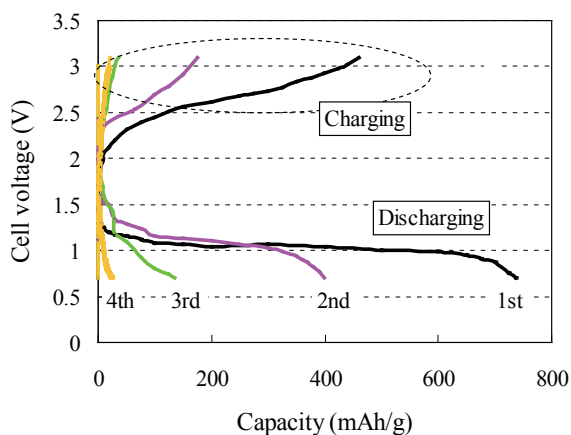


Fig. 6 Cyclic performance of non-aqueous Mg-O₂ battery with PTMA in the cathode at 60°C.

changed during the charging process, the cell voltage increased rapidly to ca. 2.0 V, followed by a more gradual rate of increase. The initial cycle charging capacity was 460 mAh/g and the reversibility against discharging was 62.4%. The charging process was associated with complexation of the PTMA with ClO₄⁻ (48 mAh/g) and the decomposition of MgO. In the second discharge, the battery showed two steps in cell voltage. The first stage, near 1.5 V, was due to the reduction of PTMA⁺ClO₄⁻, showing the performance of the radical battery, while the second stage demonstrated the discharge capacity of the Mg-O₂ battery. In the second cycle, the discharge capacity was 399 mAh/g and the charging capacity was as high as 175 mAh/g. As shown in Fig. 6, the Mg-O₂ battery exhibited rechargeable behavior over several discharge/charge cycles.

The cathode and anode potentials, and the cell voltage for the Mg-O₂ battery during the first cycle are shown in **Fig. 7**. The cathode potential during discharge was initially 2.9 V vs. Li⁺/Li, which indicates a four-electron reduction per mole of oxygen. The anode potential was ca. 1.7 V vs. Li⁺/Li, which is higher than the theoretical value calculated from the potential of Mg²⁺/Mg (0.67 V vs. Li⁺/Li). The evident drop in voltage was due to the formation of an SEI layer on the Mg anode. When the polarity of the current was reversed, the cell voltage increased up to the charging capacity of 364 mAh/g, which represents 65.7% of the discharge capacity, while the potential of the cathode

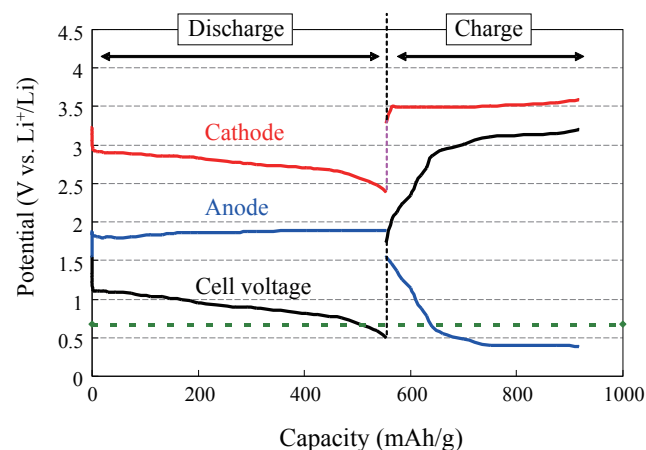


Fig. 7 Potential profiles for cathode and anode during the first cycle. The black, red and blue lines correspond to the cell voltage and the potentials of the cathode and anode, respectively. The green dotted line represents the Mg²⁺/Mg potential.

was constant at 3.5 V. These results indicate oxidation of the polymer ($\text{PTMA} + \text{ClO}_4^- + e^- \rightarrow \text{PTMA} + \text{ClO}_4^-$). The capacity due to the redox couple of the TEMPO unit was 48 mAh/g and was determined by the amount of PTMA in the cathode. Therefore, the associated turnover number was 7.6. The anode potential during charge fell below 0.67 V vs. Li^+/Li , which indicates that the deposition of Mg^{2+} occurred at the Mg anode, and thus confirms the rechargeable behavior at the Mg anode.

4. Conclusion

To date, the non-aqueous Mg-O₂ battery has been accepted as only a primary cell. We have succeeded in charging a non-aqueous Mg-O₂ battery using a redox-mediator as an O₂-electrode catalyst. Two redox-mediators have been presented for the realization of a secondary Mg-O₂ battery. One is the iodine-DMSO molecular complex, which has been investigated extensively for the past several decades. Our work has revealed a new application for the molecular complexes, i.e., as a catalyst for the decomposition of MgO. The other redox-mediator is the TEMPO compound, which has been studied as positive active material. In this study we showed the potential of TEMPO as a catalyst for MgO decomposition. The basic mechanism for electrochemical charging with the use of redox-mediators could be exploited to design multivalent metal-O₂ batteries.

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Research Field:

- Electrochemistry

Academic Degree: Dr.Eng.

Academic Societies:

- The Society of Polymer Science, Japan

- The Electrochemical Society of Japan



Figs. 2 and 4

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Figs. 6 and 7

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