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Room temperature rechargeable magnesium batteries with sulfur-containing composite cathodes prepared from elemental sulfur and bis(alkenyl) compound having a cyclic or linear ether unit

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Abstract

Room temperature rechargeable magnesium (Mg) batteries are constructed from Mg as a negative material, sulfur (S)-containing composite prepared from elemental sulfur and the bis(alkenyl) compound having a crown ether unit (BUMB18C6) or linear ether unit (UOEE) as a positive material and the simple electrolyte (0.7 mol dm^{-3} $\text{Mg}[\text{N}(\text{SO}_2\text{CF}_3)_2]_2$ -triglyme (G3) solution). The reaction between molten S and the bis(alkenyl) compound (BUMB18C6 or UOEE) provides the sulfur-containing composite, S-BUMB18C6 or S-UOEE. Both of the sulfur-containing composites are electrochemically active in the Mg salt-based electrolyte, acetonitrile- or G3- $\text{Mg}[\text{N}(\text{SO}_2\text{CF}_3)_2]_2$ electrolyte. The first discharge capacity of the test cells with the sulfur-containing composite is 460 Ah kg^{-1} (per the weight of sulfur in the composite) with the S-BUMB18C6 electrode and 495 Ah kg^{-1} with the S-UOEE electrode. According to the continuous charge-discharge cycle tests (at 10th cycle), the discharge capacity of the test cell with the S-BUMB18C6 electrode (68.1 Ah kg^{-1}) is higher than that with the S-UOEE electrode (0.18 Ah kg^{-1}). The crown ether units in the S-BUMB18C6 composite may create ion-conducting paths in the cathode, prevent rise in the internal resistance of the cathode, and provide better cycle performance of the test cells with the S-BUMB18C6 composite electrode than that with the S-UOEE electrode.

1. Introduction

Rechargeable magnesium (Mg) battery is one of the most promising candidates for high energy storage devices because of high theoretical specific capacity of Mg (2230 Ah kg^{-1} and 3832 Ah dm^{-3}) and high natural abundance of Mg resources [1-3]. Sulfur is one of the promising candidates for rechargeable batteries' cathode materials because of its high energy density (1675 Ah kg^{-1}), low cost and natural abundance. The rechargeable battery from combination between Mg and S is one of the ideal high-energy systems. The effective electrolytes for Mg electrode, such as Grignard reagent-base electrolytes, are nucleophilic [4, 5]. Such electrolytes prevent the use of electrophilic cathode such as sulfur. Kim *et al.* have been demonstrated a proof of concept for the first rechargeable Mg-S battery in the hexamethyldisilazide magnesium chloride-based electrolyte [6]. Zhao-Karger *et al.*, have been demonstrated an application of modified electrolytes in glymes and binary solvents of glyme and ionic liquid to rechargeable Mg-S battery [7]. A cathode material that functions in a simple electrolyte is required to realize low-cost rechargeable Mg batteries.

Cathode materials for rechargeable Mg batteries have been investigated by many scientists [8]. Applications of vanadium oxide, molybdenum sulfide, molybdenum oxide, manganese oxide, and transition metal silicates to the Mg or Mg-ion batteries have been

reported. Positive active materials based on organic compounds, such as benzoquinone derivatives [9, 10], carbyne polysulfide [11], poly(aniline) [12], and disulfide compounds [13] are also investigated.

Here we report preparation of room temperature rechargeable Mg batteries which have metal Mg as a negative electrode, sulfur-containing composites as a positive active material, and triglyme-Mg[N(SO₂CF₃)₂]₂ (Mg(TFSA)₂) as a simple electrolyte. The sulfur-containing composites were prepared from elemental sulfur and bis(alkenyl) compounds which have a cyclic or linear ether unit, bis(undec-10-enoyloxymethylbenzo)-18-crown-6-ether (BUMB18C6) or undecenoic acid, oxybis (2,1-ethanediyoxy-2,1-ethane-diyl) ester (UOEE) (Fig. 1). Their performance as a cathode material for room temperature Mg secondary batteries was also investigated.

2. Experimental

2.1. Materials

All reagents were purchased and used without further purification unless otherwise stated. Detailed preparation procedure of the bis(alkenyl) compounds, BUMB18C6 and

UOEE can be found elsewhere [14].

2.2. Preparation of sulfur-containing composites, S-BUMB18C6 and S-UOEE

A typical preparation procedure of the sulfur-containing composite is as follows.

Sulfur (S_8 0.256 g, 1.0 mmol, molar ratio to bis(alkenyl)compound is 16:1) was added to a test tube equipped with a magnetic stirrer and heated at 428 K. After the sulfur melted, BUMB18C6 (0.421 g, 0.5 mmol) or UOEE (0.285 g, 0.5 mmol) was slowly added to the test tube at 428 K. The mixture was stirred for 1.5 h at 433 - 443 K. The product is referred as S-BUMB18C6-(16/1) or S-UOEE-(16/1). We used them without further purification. The sulfur-containing composites, S-BUMB18C6-(16/1) and S-UOEE-(16/1) were soluble in the conventional organic solvents, tetrahydrofuran, *N*-methyl-2-pyrrolidone, and chloroform.

1H NMR ($CDCl_3$) of S-BUMB18C6-(16/1) composite (δ , ppm from TMS): 6.92-6.79(m, 6H, Ph), 5.05 (s, 4H, Ph-CH₂-O-CO-), 4.15-4.13 (m, 8H, -CH₂-CH₂-O-Ph), 3.92-3.83 (m, 8H, -CH₂-CH₂-O-Ph), 3.20-3.05 (m, 2H, -S-CH₂-CH(-S-)-CH₂-), 3.05-2.82 (m, 4H, -S-CH₂-CH(-S-)-CH₂-), 2.50-2.25 (m, 4H, -CH₂-COO-), 1.80-1.55 (m, 4H, -CH₂CH₂-COO-), 1.50-1.10 (m, 20H, -S-CH₂-C(S-)H-CH₂-(CH₂)₅-)

^1H NMR (CDCl_3) of S-UOEE-(16/1) composite (δ , ppm from TMS): 4.26-4.19 (m, 4H, $-\text{C}(=\text{O})-\text{O}-\underline{\text{CH}_2}-\text{CH}_2-\text{O}-$), 3.73-3.60 (m, 12H, $-\text{O}-\underline{\text{CH}_2}-\underline{\text{CH}_2}-\text{O}-\underline{\text{CH}_2}-\text{CH}_2-\text{O}-\text{C}(=\text{O})-\text{CH}_2-$), 3.20-2.85 (m, 2H, $-\text{S}-\text{CH}_2-\underline{\text{CH}}(-\text{S})-\text{CH}_2$, m 4H, $-\text{S}-\underline{\text{CH}_2}-\text{CH}(-\text{S})-\text{CH}_2$), 2.38-2.29(m, 4H, $-\text{CH}_2-\underline{\text{CH}_2}-\text{COO}-\text{CH}_2-$), 1.67-1.50 (m, 4H, $-\underline{\text{CH}_2}-\text{CH}_2-\text{COO}-\text{CH}_2-$), 1.45-1.22 (m, 20H, $-\text{CH}_2-(\underline{\text{CH}_2})_5-\text{CH}_2-\text{CH}_2-\text{COO}-$)

2. 3 Measurements

^1H NMR spectra of the composites were recorded on an NMR spectrometer (JNM-Lamda500, JEOL) at room temperature (*ca.* 298 K). Molecular weight of the composites was measured with a Shimadzu Prominence system equipped with a column of Shodex GPC KF-804 L (Showa Denko, column size $8.0\phi \times 300 \text{ mm} \times 2$ (in series)). Tetrahydrofuran was used as the eluent at a flow rate of 1 ml min^{-1} . From the GPC results, the molecular weight was determined as calibrated with poly(styrene) standards. Electrochemical measurements were performed with a three-electrode cell. The electrolyte contained 0.3 mol dm^{-3} (in acetonitrile for CV measurements), and 0.7 mol dm^{-3} (in triglyme for CV measurements) $\text{Mg}[\text{N}(\text{SO}_2\text{CF}_3)_2]_2$, $\text{Mg}(\text{TFSA})_2$. An S-BUMB18C6-(16/1) electrode sheet was prepared by mixing the composite, Ketjenblack (EC-600 JD, Lion) as the conductive additive, and

poly(tetrafluoroethylene) (F-104, Daikin Industries) as the binder in a weight ratio of 6:3:1. The sheet was pressed onto a stainless steel mesh current collector at 443 K and 283 kg cm^{-2} for *ca.* 10 s. The pressed sheet was cut into required size and used for electrochemical measurements. The circle-cut composite sheet (ϕ 6 mm in diameter) was used as the working electrode. The quasi-reference electrode was a Mg wire (ϕ 1.6 mm) and the counter electrode was a Pt plate (20 mm by 20 mm, 0.1 mm thickness). All of the cyclic voltammetric measurements using the three-electrode cell configuration were performed with a computer-controlled potentiogalvanostat (HZ-7000, Hokuto Denko) under Ar atmosphere (dew point was under 203 K) at 301 K. The voltammograms are normalized by the weight of the sulfur in the electrodes. A coin type test cell (size 2032) was constructed with positive electrode, a Mg foil, the electrolyte, $0.5 \text{ mol dm}^{-3} \text{ Mg(TFSA)}_2$ in acetonitrile or $0.7 \text{ mol dm}^{-3} \text{ Mg(TFSA)}_2$ in triglyme and a separator (CelgardTM 2500). The constant current charge/discharge cycle test was conducted with a charge-discharge cycler (HJ1001SD8, Hokuto Denko) at rate of 0.01 C ($1\text{C} = 1675 \text{ A kg}^{-1}$ per the weight of sulfur in the electrode) between 0 V and 3.0 V. The capacity of the test cells is normalized by the weight of sulfur in the positive electrode unless otherwise stated.

3. Results and discussion

3.1 Properties of sulfur-containing composites, S-BUMB18C6-(16/1) and S-UOEE-(16/1)

Fig. 1 shows the structure of bis(alkenyl) compounds, bis(undec-10-enoyloxymethylbenzo)-18-crown-6-ether (BUMB18C6) and undecenoic acid, oxybis (2,1-ethanediylxy-2,1-ethane-diyl) ester (UOEE). The sulfur-containing composite, S-BUMB18C6-(16/1) or S-UOEE-(16/1) were prepared by heating the mixture of elemental sulfur and the bis(alkenyl) compound, BUMB18C6 or UOEE. Disappearance of double bonds in the BUMB18C6 and UOEE molecules was confirmed from ^1H NMR data of the resulted composites. The reaction for preparation of the sulfur-containing composites is initiated by S_8 ring opening reaction and the resulted biradicals react with alkenyl compounds [15-17]. The resulted sulfur-containing composites were soluble in conventional organic solvents, such as tetrahydrofuran, chloroform, and *N*-methyl-2-pyrrolidone which are poor solvents for elemental sulfur. The high solubility of the composites suggests that the loaded sulfur to the test tube was incorporated into the sulfur-containing composite, S-BUMB18C6-(16/1) or S-UOEE-(16/1) composite. The GPC profiles of the S-BUMB18C6-(16/1) and S-UOEE-(16/1) composites had over-lapped peaks as listed in Table 1. The distribution

of molecular weight of the S-BUMB18C6 composite was estimated to be 650 – 2770 and that of the S-UOEE-(16/1) composite was 706 – 6490 from GPC results. Fig. 2 (a) shows the estimated structures of the S-BUMB18C6-(16/1) and S-UOEE-(16/1) composites from the results of ^1H -NMR and GPC measurements. The theoretical capacity of S-BUMB18C6-(16/1) or S-UOEE-(16/1) composites is estimated at 555 Ah kg^{-1} or 694 Ah kg^{-1} under the assumption that the sulfur is completely reacted with the bis(alkenyl) compound and included into the composite. The value of the S-BUMB18C6-(16/1) composite is calculated as below (see Fig. 2(b)).

- (1) All of the double bonds in the BUMB18C6 react with sulfur and C-S bonds are created in the composite.
- (2) Other sulfur atoms form polysulfide chains ($-\text{S}_n-$) and the polysulfide chains link with the C-S bonds in the BUMB18C6.
- (3) Two-types electrochemical reduction of the sulfur-containing composite is estimated. One is the reduction of the sulfur atom which links with carbon (from $\text{C-S} + e$ to C-S^- , e means electron) and another is the reduction of the sulfur atoms in the polysulfide chains (from $-\text{S}_n- + 2ne$ to $n\text{S}^{2-}$).
- (4) The average unit structure of the S-BUMB18C6-(16/1) composite has one BUMB18C6 molecule and 16 sulfur atoms and the molecular weight of the average unit

is 1353 ($841+32\times 8\times 2 = 1353$).

(5) The total number of the electrons for the reduction of the unit is 28 ($1e\times 4 + 2e\times 12 = 28e$).

$$\text{Estimated theoretical capacity (Ah kg}^{-1}\text{)} = (F\times 28 / 3600/1353)\times 1000 \quad (1)$$

where F is faraday constant.

The theoretical capacity of the S-UOEE-(16/1) composite is also estimated from similar procedure.

3. 2. Electrochemical properties of sulfur-containing composite in an organic liquid electrolyte

Electrochemical reactivity of the sulfur-containing composites in organic electrolytes with lithium salts can be found elsewhere [14]. **Fig. 3 (a)** shows the cyclic voltammograms of the S-BUMB18C6-(16/1) electrode in $0.3 \text{ mol dm}^{-3} \text{ Mg}(\text{TFSA})_2$ in acetonitrile at a scan rate of 5 mV s^{-1} . At 1st cathodic scan from the rest potential, increase of current density was observed from 0.74 V *vs.* quasi -Mg electrode (Mg_{quasi}) in the acetonitrile-based electrolyte solution. In anodic scan anodic current peak around 0.94 V *vs.* Mg_{quasi} was observed. The shape of the voltammogram at 2nd scan was similar as that at 1st scan. This suggests that the redox reaction of the

S-BUMB18C6-(16/1) in acetonitrile with $\text{Mg}(\text{TFSA})_2$ is reversible.

Fig. 3(b) shows the cyclic voltammograms of the S-UOEE-(16/1) composite electrode in the acetonitrile electrolyte. The voltammograms are very similar to those of the S-BUMB18C6-(16/1) electrode. This indicates that the electrochemical reaction of the S-UOEE-(16/1) composite is similar as that of the S-BUMB18C6 composite.

Fig. 3(c) shows S-BUMB18C6-(16/1) electrode in $0.7 \text{ mol dm}^{-3} \text{ Mg}(\text{TFSA})_2$ in triglyme at a scan rate of 0.5 mV s^{-1} . The shape of the voltammograms at slower scan rate (0.5 mV s^{-1}) is similar as that in acetonitrile electrolyte (**Fig.3 (a)**). No obvious peak was observed at the scan rate of 5 mV s^{-1} . The observation of the responses at slower scan rate indicates that the redox reaction of the S-BUMB18C6-(16/1) electrode in the triglyme electrolyte is slower than that in the acetonitrile electrolyte. Self-diffusion coefficients of Mg^{2+} cation and TFSA^- anion in glyme-based electrolytes (diglyme and tetraglyme) are lower than those in acetonitrile-based electrolytes [18]. Thus the electrochemical responses in glyme-based electrolyte were only observed at slower scan rates (0.5 mV s^{-1}). **The S-UOEE-(16/1) electrode in the glyme-based electrolyte showed the similar electrochemical behavior of the S-BUMB18C6 electrode (Fig. 3 (d)).**

Electrochemical reduction of sulfur in lithium ion-based electrolyte systems shows the multi-step reaction (four reduction steps) [19]. All of the cyclic voltammograms of

the sulfur-containing composites in the $\text{Mg}(\text{TFSA})_2$ electrolytes did not show such multi-step reduction responses. This suggests that electrochemical reaction in the Mg-sulfur system is not similar to that in the Li-sulfur systems. Further investigations are required to clarify the reaction mechanism of the sulfur-containing composites in the Mg electrolytes.

3. 3. Charge-discharge behavior of Mg-sulfur containing composite test cells

The coin (2032 size) cells were constructed using the sulfur-containing composite electrode as a positive electrode, a Mg plate as a negative electrode, and 0.5 mol dm^{-3} $\text{Mg}(\text{TFSA})_2$ -acetonitrile solution or 0.7 mol dm^{-3} $\text{Mg}(\text{TFSA})_2$ -triglyme solution as the electrolyte. Fig. 4(a) shows the charge-discharge curves of the Mg|S-BUMB18C6-(16/1) test cell with the acetonitrile electrolyte under constant current condition, 0.01 C ($1\text{C} = 1675 \text{ A kg}^{-1}$ per the weight of the sulfur in the electrodes). The voltage plateau at 0.54 V was observed in the discharge profile. The cell delivers 608 Ah kg^{-1} initial discharge capacity and 23 Ah kg^{-1} at 10th discharge. This capacity reduction is due to low efficiency of plating of Mg in the $\text{Mg}(\text{TFSA})_2$ -acetonitrile electrolyte [20].

Fig. 4 (b) shows the charge-discharge curves of the Mg|S-BUMB18C6-(16/1) test cell

with the triglyme electrolyte. The cell delivers 460 Ah kg^{-1} initial discharge capacity and 68.1 Ah kg^{-1} 10th discharge capacity. The cell with the triglyme-base electrolyte preserved higher capacity than that with the acetonitrile-base electrolyte. It is due to electrochemical activity and reversibility of the sulfur-containing composite and high efficiency of plating and stripping of Mg in the triglyme electrolyte [21]. Fig. 4 (c) shows the charge-discharge profiles of the Mg|S-UOEE-(16/1) test cell with the triglyme electrolyte. The cell delivers 495 Ah kg^{-1} initial discharge capacity and 0.18 Ah kg^{-1} 10th discharge capacity (not seen in Fig. 4(c)). Rapid decrease in capacity of the Mg|S-UOEE-(16/1) test cell was observed. Initial discharge capacity based on the weight of the sulfur-containing composite of both of the test cells was 174 Ah kg^{-1} (per weight of the S-BUMB18C6-(16/1) composite) and 234 Ah kg^{-1} (per weight of the S-UOEE-(16/1) composite). These values are almost equal to about 30 % of their theoretical capacity estimated in Section 3.1.

Fig. 4(d) shows the variation of discharge capacity of the test cell with the S-BUMB18C6-(16/1) or S-UOEE-(16/1) composite electrode with charge-discharge cycle number. The decrease rate of the capacity of the Mg|S-BUMB18C6-(16/1) cell with charge-discharge cycle was slower than that of the Mg|S-UOEE-(16/1) cell. Cycling behavior of the cell with the S-BUMB18C6-(16/1) electrode was better than

that with the S-UOEE-(16/1) electrode. The start voltage at 1st charge cycle of the cell with the S-BUMB18C6-(16/1) electrode was 0.422 V and that with the S-UOEE-(16/1) electrode was 0.427 V. The start voltage at 10th cycle of the cell with the S-BUMB18C6-(16/1) electrode was 0.694 V and that with the S-UOEE-(16/1) electrode was 1.258 V. This indicates that the internal resistance of the S-UOEE-(16/1) electrode at 10th cycle become higher than that of the S-BUMB18C6-(16/1) electrode at 10th cycle. Crown ether units have been used as conductance enhancers for solid polymer electrolyte systems [22, 23]. Their enhancing mechanism is explained that (1) assistance of ion motion by formed ionophore [22], (2) the chain-like formation in the complexes[23], (3) increased amorphous phase[23] and/or (4) the enhanced free volume[23]. Formation of some amount of ion conducting paths in the cathode by the cyclic ether units and Mg ions maintains the performance of the cells with the S-BUMB18C6-(16/1) composite cathode. Further experiment for test of the Mg|sulfur-containing composite electrode cells under various conditions is planned to be conducted in near future.

4. Conclusion

We have investigated preparation and characterization of sulfur-containing

composites synthesized from sulfur and bis(alkenyl) compound with a crown ether or linear ether unit. The sulfur-containing composites showed the electrochemical responses in the acetonitrile and triglyme electrolyte solutions. Electrochemical reaction rate of the sulfur-containing composite electrode in the acetonitrile electrolyte is faster than that in the triglyme electrolyte. The test cells constructed from a Mg plate, the sulfur-containing composite electrode, and simple triglyme-based electrolyte. Cycling behavior of the cell with the sulfur-containing composite electrode which has a cyclic ether unit was better than that which has a linear ether unit. This may be due to formation of the ion conducting paths in the cathode by the cyclic ether units and Mg ions. The produced paths prevent rise in the internal resistance of the cathode.

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Figure captions

Fig. 1 Structures of the bis(alkenyl) compounds, BUMB18C6 and UOEE.

Fig. 2 (a) Structures of the sulfur-containing composites, S-BUMB18C6 and S-UOEE and (b) reaction scheme of electrochemical reduction of the sulfur-containing composites, S-BUMB18C6-(16/1) and S-UOEE-(16/1).

Fig. 3 Cyclic voltammograms of the sulfur-containing composite electrode (a) S-BUMB18C6-(16/1) electrode and (b) S-UOEE-(16/1) electrode in 0.3 mol dm^{-3} Mg(TFSA)₂-acetonitrile electrolyte (scan rate at 5 mV s^{-1}), and (c) cyclic voltammograms of the S-BUMB18C6-(16/1) electrode and (d) S-UOEE-(16/1) electrode in 0.7 mol dm^{-3} Mg(TFSA)₂-triglyme electrolyte (scan rate at 0.5 mV s^{-1}).

Fig. 4 (a) Charge-discharge profiles of the test cell, Mg|S-BUMB18C6-(16/1) cell with 0.5 mol dm^{-3} Mg(TFSA)₂-acetonitrile electrolyte, (b) Mg|S-BUMB18C6-(16/1) cell and (c) Mg|S-UOEE-(16/1) cell with 0.7 mol dm^{-3} Mg(TFSA)₂-triglyme electrolyte, charge-discharge rate was 0.01C ($1\text{C} = 1675 \text{ A kg}^{-1}$ per weight of the sulfur in the electrode), and cutoff voltage was 0 V and 3 V ; and (d) variation of discharge capacity

of the test cell, Mg|S-BUMB18C6-(16/1) and Mg|S-UOEE-(16/1) cell, with cycle number, experimental condition is presented in Fig. 4(b) and (c).

Table 1 Peak list of the GPC profile of the sulfur-containing composite, S-BUMB18C6-(16/1) and S-UOEE-(16/1)

S-X-(16/1) X	Molecular weight at peak top ^{a)} (percentage of the fraction) ^{b)}
BUMB18C6	2770 (48.3), 1470 (23.9), 990 (14.0), 650 (13.8)
UOEE	6490 (26.1), 3430 (15.7), 2210 (24.0), 1450 (4.1), 955 (23.7), 706 (6.6)

a) The molecular weight is calibrated with poly(styrene) standards.

b) The percentage of the molecular weight fraction in the composite is estimated from absorbance on the UV detector (at 254 nm).

BUMB18C6

UOEE

Figure(s)

Figure(s)

Figure(s)

Figure(s)

Figure(s)

Figure(s)

Figure(s)

Figure(s)

Figure(s)