Non-aqueous liquid electrolyte based magnesium perchlorate/dimethyl sulfoxide for rechargeable magnesium battery

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ABSTRACT

Non aqueous liquid electrolyte system based dimethyl sulfoxide, tetraethylene glycol dimethyl ether (DMTG) and magnesium perchlorate (Mg(ClO₄)₂) is synthesized via ‘Solvent-in-Salt’ method for the application in magnesium battery. Impedance spectroscopy, dielectric properties, and ion transport were used to characterize the nature of conduction process. The conductivity conformation with the addition of (Mg(ClO₄)₂) can be explained on the basis of dissociation of ion aggregates formed in electrolytes at higher concentrations of the salt. The ionic conductivity of the electrolyte increased with addition of salt reached to the highest conductivity value of \( \approx 10^{-3} \text{ S/cm} \) at 0.22 M Mg(ClO₄)₂. The frequency dependence of conductivity obeys special power law. The estimated value of Mg\(^{2+}\) ion transference number is found to be 0.68 for high conducting film. A prototype cell was constructed using the non-aqueous liquid electrolyte with Mg anode and TiO₂ cathode. The Mg/ TiO₂ cell shows promising cycling. The discharge characteristics are found to be satisfactory as a laboratory cell. Mg intercalation into TiO₂ was confirmed by energy dispersive X-ray spectroscopy (EDS).

Keywords: Non-aqueous liquid electrolyte; Ionic conductivity; Magnesium battery.

1 INTRODUCTION

With the increase in global energy demand, development of high energy density, economy, and environmental friendly rechargeable batteries is considered a big challenge [1]. Lithium batteries have high energy density but high price due to geographically limitedness in the earth crust and unsafe [2]. To meet these challenges, paramount attention has been paid to develop alternative battery based on magnesium because it is widespread, cheap, environment-friendly and exhibit high theoretical capacity [3]. However, developing magnesium batteries faces great challenges such as incompatibility between anode and electrolyte due to the high polarizing ability. Thus, the development of an electrolyte which is stable in contact with the electrode materials, does not form a blocking layer, low cost and has a wide electrochemical window are critically required.

More efforts have been inclined to develop suitable electrolyte compatible with Mg metal and all other battery components, including the magnesium organohalolodiuminate [4], pyrrolidinium bis(trifluoromethanesulfonyl)imidide [5], organoborn magnesium salts[6], 1-ethyl-3-methylimidazolium ethyl sulfate[7], and borohydride tetraglyme [8,9] electrolytes. However, the development of rechargeable Mg batteries still hindered by using electrolyte suffer from the use of very volatile solvents such as THF, and organohalolodiuminate electrolytes with highly corrosive nature, high cost, high air sensitivity, and low anodic stability which limit the choice of cathodes [1].

Magnesium perchlorate is a powerful oxidizing agent, fast conducting and it was believed that the non-aqueous electrolytes consisting of magnesium perchlorate in acetonitrile solvent were capable of overcoming some obstacles [10]. Furthermore, Dimethyl sulfoxide (DMSO) is an organosulfur compound with Melting point 19 °C and Boiling point 189 °C and the formula (CH₃)₂SO. This colorless liquid is an important polar aprotic solvent that dissolves both polar and nonpolar compounds and is miscible in a wide range of organic solvents as well as water. Accordingly, electrolyte design focused on overcoming traditional solvent problems by using dimethyl sulfoxide DMSO as a new solvent for Mg battery which nonvolatile and may improve anodic stability.

Upon the above considerations, a key obstacle to obtain the better performance, nonvolatile new electrolyte system for rechargeable magnesium batteries should be developed. Herein, new classes of non-aqueous liquid ‘Solvent-in- Salt’ electrolytes, DMTG/Mg(ClO₄)₂ were prepared. The electrolytes were characterized by using impedance spectroscopy and ion transference. Mg/TiO₂ cell was assembled using the electrolyte that shows optimum behaviors, and its cycling performances will be briefly examined to evaluate the applicability of the electrolyte to solid-state magnesium batteries. Elemental mapping of TiO₂ cathode was measured before and after cycling.

2 EXPERIMENTAL SECTION

All tested electrolytes consisted of a magnesium perchlorate (alfa aser) with different concentrations, \( x = 0.0, \ldots, 2.5 \text{ g in dimethyl sulfoxide (Loba Chemie) (30 ml) and tetraethylene glycol dimethyl ether(Aldrich, 99.9\%) (20 ml) (DMTG). The resulting solutions were stirred for 2 hours at room temperature.}
Conductivity measurements of DMTG/Mg(ClO$_4$)$_2$ electrolyte were performed using impedance method. Electrolyte samples were put into a conductivity cell between two similar aluminum electrodes. The whole assembly was placed in a furnace monitored by a temperature controller. The rate of heating was adjusted to be 2 K min$^{-1}$. Impedance measurements were performed on Gwinstek LCR-8110G in the frequency ranging from 20 Hz to 10 MHz at different temperatures.

Magnesium transference number (tMg$^{2+}$) for DMTG/Mg(ClO$_4$)$_2$ electrolyte was measured by the steady-state technique which involved a combination of ac and dc measurements. The complex impedance response of the Mg/electrolyte/Mg cell was first measured using CH604E instrument to determine the cell resistance. It was followed by the dc polarization run, in which a small voltage pulse $\Delta V=0.3$ V was applied to the cell until the polarization current reached the steady-state.

The cathode electrodes were prepared by a slurry tape casting procedure. The slurry consisted of 70 wt% active materials (TiO$_2$), 30 wt% Graphene and 10 wt% PVA binder, dissolved in water. The slurry was tape-cast on the stainless steel rode, and then dried in a vacuum oven at 100 °C for 2 h. Entek membrane separator has been used. The whole assembly was shown in Fig. 1. The charge–discharge cycles were carried out using NEWARE BTS-TC35 with a cutoff voltage range 1.4 to 0.4 V versus Mg/Mg$^+$ at room temperature. The discharge/charge time is 2/2 hours and 10 minutes rest. The current density was 10 mA/cm$^2$.

Elemental mapping of the TiO$_2$ electrode was measured using an energy dispersive spectrometer (INCA Energy, Oxford Instruments) before and after cycling. Scanning electron microscope (SEM) was used to observe changes in the surface morphology of the TiO$_2$ electrode before and after cycling.

3 RESULTS AND DISCUSSION

Plausible reaction model between Mg(ClO$_4$)$_2$ and DMTG are shown in Fig. 2a. (Mg(ClO$_4$)$_2$) solvated or polymerized with halogen bridges and are thought to have the structure shown in Fig. 2a. According to this concept Mg exist as a dimer. The dimer is broken into monomer with coordinates solving molecules forming an ionic pair and Mg$^{2+}$ ion transfer through cation exchange between the final stable species [11-12].

![Fig. 1 Proposed reaction scheme of DMTG /Mg(ClO$_4$)$_2$ electrolyte.](image1)

![Fig. 2 Schematic design of the lab cell.](image2)
The magnesium-ion transference number was obtained by combining alternating-current (AC) impedance and direct-current (DC) polarization measurements using a symmetric Mg/electrolyte/Mg cell, Fig. 3. First, AC impedance test was performed to obtain cell resistance $R_{\text{cell}}$. Then DC polarization was carried out to obtain a stable current $I_{\text{DC}}$. The magnesium-ion transference number was calculated by the formulas ($t_{\text{Mg}} = R_{\text{cell}}/R_{\text{DC}}$ and $R_{\text{DC}} = V_{\text{DC}}/I_{\text{DC}}$) [13]. The transport number of Mg$^{2+}$ ion determined by means of a combination of d.c. and a.c. techniques is $\sim 0.61$.

Complex impedance plots of DMTG/Mg(ClO$_4$)$_2$ electrolyte at different Mg(ClO$_4$)$_2$ concentrations and temperatures are shown in Fig. 4a. The complex plot shows semicircle with tail at low frequencies which correspond to the bulk resistance $R_b$ with parallel combination of the frequency dependent capacitance $C_g$, Fig. 4a (inset). The low frequencies tail can be attributed to Warburg impedance (mass transfer at boundary of electrolyte aluminum electrode). The diameter of the semicircle decreases with increasing concentrations. The bulk resistance value $R_b$ is determined from the low frequency intercepts on the x-axis of the complex impedance plots. The ionic conductivity is calculated using the equation,

$$\sigma_b = \frac{1}{R_b} \times \frac{L}{A} \quad (1)$$

where $L$ is the thickness of the electrolyte, $A$ is the surface area of the film.

Fig. 4b shows the variation of ionic conductivity ($\sigma$) of DMTG/Mg(ClO$_4$)$_2$ electrolyte with respect to the content of Mg(ClO$_4$)$_2$. The maximum conductivity of pure DMTG is $\sim 10^{-6}$ S.cm$^{-1}$ while, for DMTG/Mg(ClO$_4$)$_2$ electrolyte (0.22 M Mg(ClO$_4$)$_2$) is $\sim 10^{-3}$ S.cm$^{-1}$ at room temperature. Conductivity-concentrations independence is observed, when the content of Mg(ClO$_4$)$_2$ salt exceed $\sim 0.16$ M. General expression of ionic conductivity can be illustrated as below,

$$\sigma = nq\mu$$

where $n$ is the number of charge carriers, $q$ is the charge of ions type, and $\mu$ is the mobility of ion pairs. The possible reason of enhancement in conductivity at low concentration of Mg(ClO$_4$)$_2$ is due generation/introduction of mobile charged species, namely Mg$^{2+}$ and Cl$^-$. The Conductivity-concentrations independence behavior, observed after $\sim 0.16$ M of Mg(ClO$_4$)$_2$, is consistent with the higher viscosities of the more concentrated salt mixtures, and thus restricted free cation mobility [14].
Fig. 5a shows the frequency dependence of the total conductivity for DMTG /Mg(ClO$_4$)$_2$ non-aqueous liquid electrolyte at different concentration of Mg(ClO$_4$)$_2$ at room temperature. Pure electrolyte shows two regions, the first region exhibited low frequency conductivity independence behavior, the second region $\omega > 30$ kHz show high frequency dispersion behavior.

High concentrations of Mg(ClO$_4$)$_2$, show reciprocal behavior where, low frequency-conductivity dispersion observed followed by independence behavior. Fig. 5b shows the frequency dependence of the total conductivity for DMTG /Mg(ClO$_4$)$_2$ (0.22 M) non-aqueous liquid electrolyte at different constant temperatures. The behavior can be expressed by the following relation:

$$\sigma_{ac}(\omega) = A_1 \omega^{n_1} + A_2 \omega^{n_2} + A_3 \omega^{n_3}$$  (3)

where $A$ is the frequency independent pre-exponential factor, $\omega$ is the angular frequency and $n_1$, $n_2$ and $n_3$ are the frequency exponent. The values of the exponents have been obtained using the least square fitting of Eq. (3) for the three regions. These values are listed in table 1. For the first region (20-800 Hz), the values of $n_1$ lie within the range of $0.4 < n_1 < 0.5$. The values of $n_1$ predicts the domination of hopping conduction in DMTG/Mg(ClO$_4$)$_2$ (M=0.22 M) electrolyte. It can be noticed that the values of $n_2$ for the second region (1 kHz-1 MHz) is $\sim 0$ (frequency independent). The theoretical approaches of this behavior may be attributed to that the carriers transport takes place through infinite percolation path that can be explained by

Fig. 6 Temperature-conductivity dependence of 0.24 M electrolyte at different frequencies.

Fig. 7 The variation of a. dielectric constant $\varepsilon'$, b. dielectric loss $\varepsilon''$ with frequency at different Mg(ClO$_4$)$_2$ concentrations.
'percolation' model [15]. The third region shows conductivity attenuation behavior with frequency and the exponent \( n_3 \) is negative. As higher frequencies, ions not being able to follow the field variation therefore, more and more charges are accumulated at the electrodes and electrode interfaces, which leads to a decrease in the number of free mobile ions and eventually a drop in conductivity at higher frequencies[9,16].

The effect of temperature on the ionic conductivity of the selected electrolyte (0.22 M) was studied. The temperature dependence of ac conductivity of DMTG/Mg(ClO\(_4\))\(_2\) electrolyte is of the Arrhenius type:

\[
\sigma = \sigma_o \exp \left( \frac{-E_a}{KT} \right)
\]

where \( \sigma_o \) in Eq. 4 is a pre-exponential factor, \( E_a \) is the activation energy, \( K \) is the Boltzmann constant and \( T \) is the temperature in Kelvins. Fig.6 shows \( \ln(\sigma) \) versus \( 1000/T \) plots at different constant frequencies. The results are tabulated in table 1. The values of activation energy increase with increasing frequency, which may be due to the inability of charge carriers to follow rapid frequencies. Fig.7 a and b show plot of dielectric constant \( \varepsilon' \) and dielectric loss \( \varepsilon'' \) as a function of frequency at different concentrations, respectively. For all concentrations, frequency dispersion is observed in the low frequency range followed by nearly frequency independent behavior. The same behavior is observed for plot of \( \varepsilon' \) and \( \varepsilon'' \) as a function of frequency at different temperatures for 0.22 M Mg(ClO\(_4\))\(_2\) (Fig.8 a and b). The low frequency dispersion is attributed to material electrode polarization effect and thus confirming that electrolyte in this study are ionic conductors. Generally, according to Debye relations, the decrease of \( \varepsilon' \) and \( \varepsilon'' \) with frequency can be associated to the inability of dipoles to rotate rapidly leading to a lag between frequency of oscillating dipole and that of the applied field. While, the material electrode interface polarization of the composites masks the other relaxation processes at low frequencies [17-18].

### 3.4 Battery characterization

To check the compatibility of electrolytes containing the 0.22 M Mg(ClO\(_4\))\(_2\) complex with Mg\(^{2+}\) ion intercalation cathodes, prototype tube cell was assembled using Mg ribbon anode and TiO\(_2\) cathode. Firstly, discharge-charge cycle was operated to collect non-magnesium ion conducting surface films composed at Mg surface. After, we replace this magnesium ribbon (anode) by another fresh to build the rechargeable tube cell. Fig. 9 presents its typical potential time profile with the discharge and charge time limits of 2/2 hours. The cell demonstrates reversible cycling behavior at current density \( \sim 10 \) \( \mu \)A/cm\(^2\) with constant profile. The cycling tests suggest minimal capacity fade upon cycles (Fig. 9).

The well-defined charge-discharge profiles suggest a highly reversible intercalating behavior of Mg\(^{2+}\) ions in the electrolyte into TiO\(_2\) cathode. These results clearly suggest that DMTG/Mg(ClO\(_4\))\(_2\) complex based electrolyte can be incorporated into rechargeable Mg batteries.

Fig. 10 a and b show the morphological effect of the electrochemical process on the surface of TiO\(_2\) cathode. The relevant EDS spectrum was printed at the bottom of each image. Prior to the characterization, TiO\(_2\) cathode was soaked and washed several times to remove electrolyte.
From these figures, the cathode surface became smooth after cycling compared to the rough surface of the pristine electrode (before cycling). The EDS spectrum indicates the ratio of Ti, O and Mg elements and the data are illustrated in table 2. EDS results indicate that the amount of Mg increases from 0 to 7.2 wt.% before and after cycling, respectively. Increasing of Mg means that the electrolyte allows the flow of Mg ions, from anode to cathode [19].

The chemical reaction that probably takes place at the cathode is,

\[ TiO_2 + xMg(II) + 2xe \rightleftharpoons Mg_xTiO_2 \]

That is, during the first discharge, Mg\(^{2+}\) ion is inserted into TiO\(_2\) structure from DMTG /Mg(ClO\(_4\))\(_2\) electrolyte, and deserted from to electrolyte during the recharge.

4 CONCLUSION

In conclusion, DMTG /Mg(ClO\(_4\))\(_2\) non aqueous liquid electrolyte has been established. This new electrolyte possesses comparable high excellent reversibility and compatibility with TiO\(_2\) cathode suggests this electrolyte has great potential for rechargeable magnesium batteries. In addition, the synthetic concept herein opens up a new alternative option for the development of promising rechargeable magnesium batteries.

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REFERENCES

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