

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

E. Sheha

Physics Department, Faculty of Science, Benha University,
Benha 13518, Egypt
Email: ISLAM.SHIHAH@fsc.bu.edu.eg,
Tel: +201007414705

ABSTRACT

Non aqueous liquid electrolyte system based dimethyl sulfoxide, tetraethylene glycol dimethyl ether (DMTG) and magnesium perchlorate ($\text{Mg}(\text{ClO}_4)_2$) 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 ($\text{Mg}(\text{ClO}_4)_2$) 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 $\approx 10^{-3} \text{ S.cm}^{-1}$ at 0.22 M $\text{Mg}(\text{ClO}_4)_2$. The frequency dependence of AC 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 TiO_2 cathode. The Mg/ TiO_2 cell shows promising cycling. The discharge characteristics are found to be satisfactory as a laboratory cell. Mg intercalation into TiO_2 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.

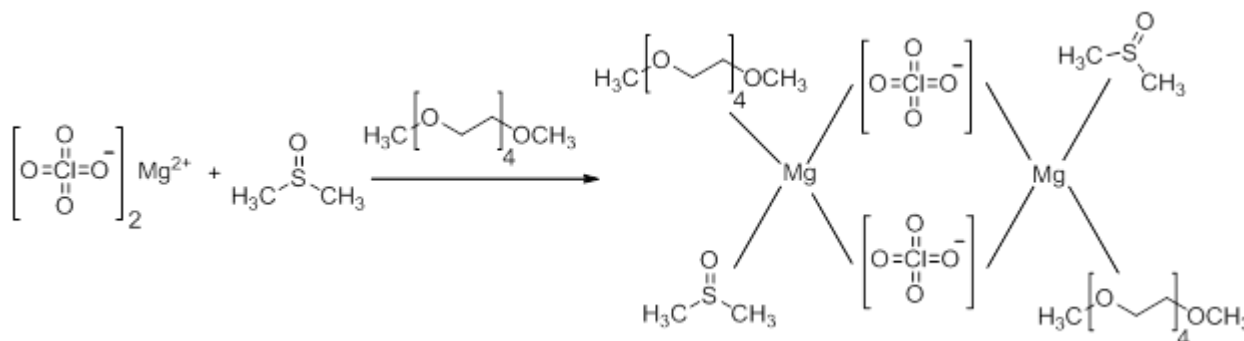
More efforts have been inclined to develop suitable electrolyte compatible with Mg metal and all other battery components, including the magnesium organohaloaluminate [4], pyrrolidinium bis(trifluoromethanesulfonyl)imide [5], organoborn magnesium salts[6], 1-ethyl-3-methylimidazolium ethyl sulfate[7], 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 organohaloaluminate electrolytes with highly corrosive nature, high cost, high air sensitivity, and low anodic stability which limit the choice of cathodes [9].

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 $(\text{CH}_3)_2\text{SO}$. 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/ $\text{Mg}(\text{ClO}_4)_2$ were prepared. The electrolytes were characterized by using impedance spectroscopy and ion transference. Mg/ TiO_2 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 TiO_2 cathode was measured before and after cycling.

2 EXPERIMENTAL SECTION

All tested electrolytes consisted of a magnesium perchlorate (alfa aser) with different concentrations, $x = 0.0, \dots, 2.5 \text{ g}$ 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.

Plausible reaction model between $\text{Mg}(\text{ClO}_4)_2$ andFig. 1 Proposed reaction scheme of DMTG / $\text{Mg}(\text{ClO}_4)_2$ electrolyte.

Conductivity measurements of DMTG/ $\text{Mg}(\text{ClO}_4)_2$ 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-811OG in the frequency ranging from 20 Hz to 10MHz at different temperatures.

Magnesium transference number ($t_{\text{Mg}^{2+}}$) for DMTG/ $\text{Mg}(\text{ClO}_4)_2$ 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 $\Delta V=0.3\text{V}$ 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 rod, 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/cm². 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.

DMTG are shown in Fig. 2 a. ($\text{Mg}(\text{ClO}_4)_2$) 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].

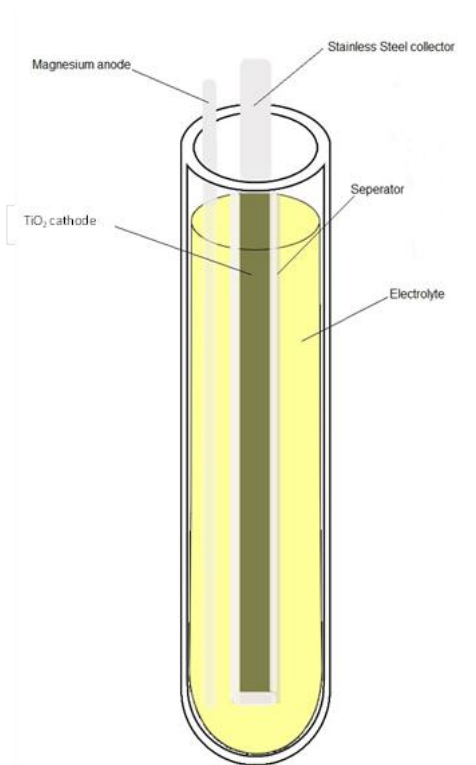


Fig.2 Schematic design of the lab cell.

3 RESULTS AND DISCUSSION

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_{cell} . Then DC polarization was carried out to obtain a stable current I_{DC} . The magnesium-ion transference number was calculated by the formulas ($t_{Mg} = R_{cell}/R_{DC}$ and $R_{DC} = V_{DC}/I_{DC}$) [13]. The transport number of Mg^{2+} ion determined by means of a combination of d.c. and a.c. techniques is ~ 0.61 .

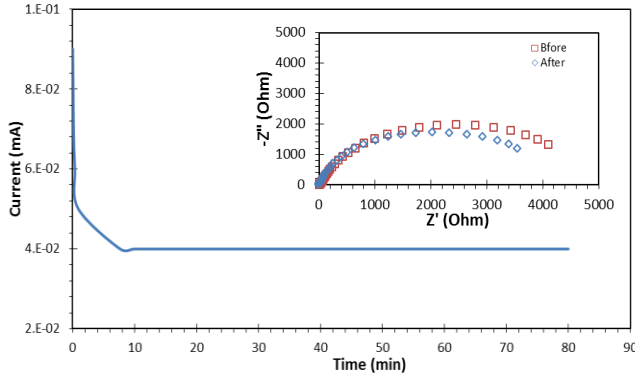


Fig.3 Polarization current against time and inset Cole-Cole plot before and after polarization of Mg/ 0.22 M $Mg(ClO_4)_2$ /Mg cell.

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 (σ) of DMTG/ $Mg(ClO_4)_2$ electrolyte with respect to the content of $Mg(ClO_4)_2$. The maximum conductivity of pure DMTG is $\sim 10^{-6} \text{ S.cm}^{-1}$ while, for DMTG/ $Mg(ClO_4)_2$ electrolyte (0.22 M $Mg(ClO_4)_2$) is $\sim 10^{-3} \text{ S.cm}^{-1}$ at room temperature. Conductivity-concentrations independence is observed, when the content of $Mg(ClO_4)_2$ salt exceed $\sim 0.16 \text{ M}$. General expression of ionic conductivity can be illustrated as below,

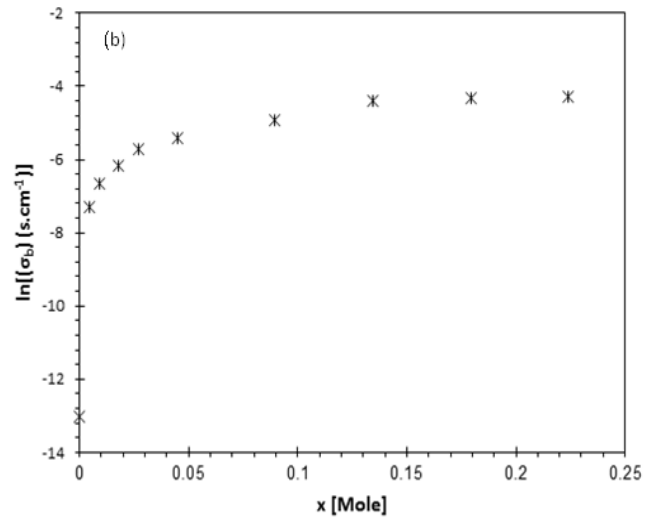
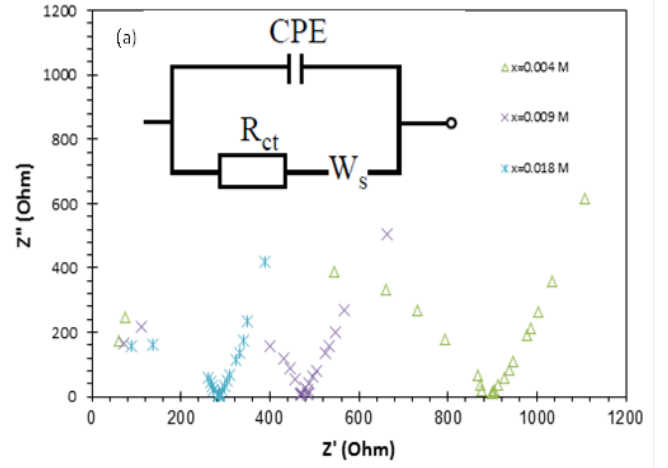


Fig. 4 a. Cole-Cole plots of DMTG/ $Mg(ClO_4)_2$ electrolyte b. Variation of ionic conductivity of electrolyte with $Mg(ClO_4)_2$ concentration.

$$\sigma = nq\mu \quad (2)$$

where n is the number of charge carriers, q is the charge of ions type, and μ 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 $\sim 0.16 \text{ M}$ 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(ClO₄)₂ non-aqueous liquid electrolyte at different concentration of Mg(ClO₄)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.

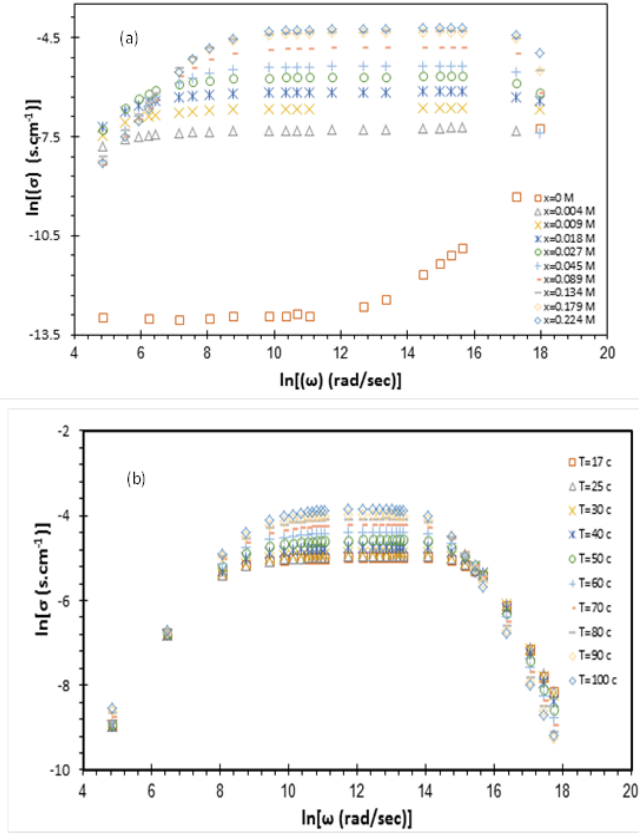


Fig.5 a. Frequency dependence of ionic conductivity for electrolyte at different Mg(ClO₄)₂ concentration, b. Frequency dependence of ionic conductivity for x=0.24 M electrolyte at different temperatures.

High concentrations of Mg(ClO₄)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(ClO₄)₂ (0.22 M) non-aqueous liquid electrolyte at different constant temperatures. The behavior can be expressed by the following relation:

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

where A is the frequency independent pre-exponential factor, ω 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(ClO₄)₂ (M=0.22 M) electrolyte. It can be noticed that the values of n_2 for the

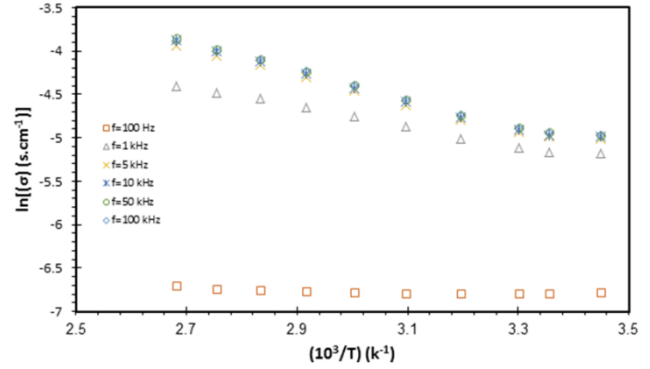


Fig. 6 Temperature-conductivity dependence of 0.24 M electrolyte at different frequencies.

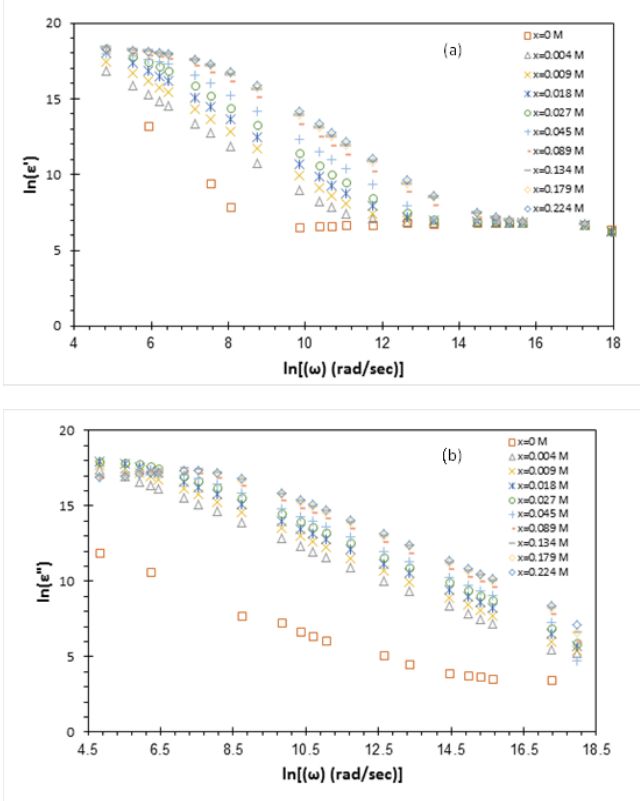


Fig. 7 The variation of a. dielectric constant ϵ' , b. dielectric loss ϵ'' with frequency at different Mg(ClO₄)₂ concentrations.

second region (1kHz-1MHz) is ~ 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

'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(ClO₄)₂ electrolyte is of the Arrhenius type:

$$\sigma = \sigma_o \exp\left(\frac{-E_a}{KT}\right) \quad (4)$$

where σ_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 ϵ' and dielectric loss ϵ'' 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

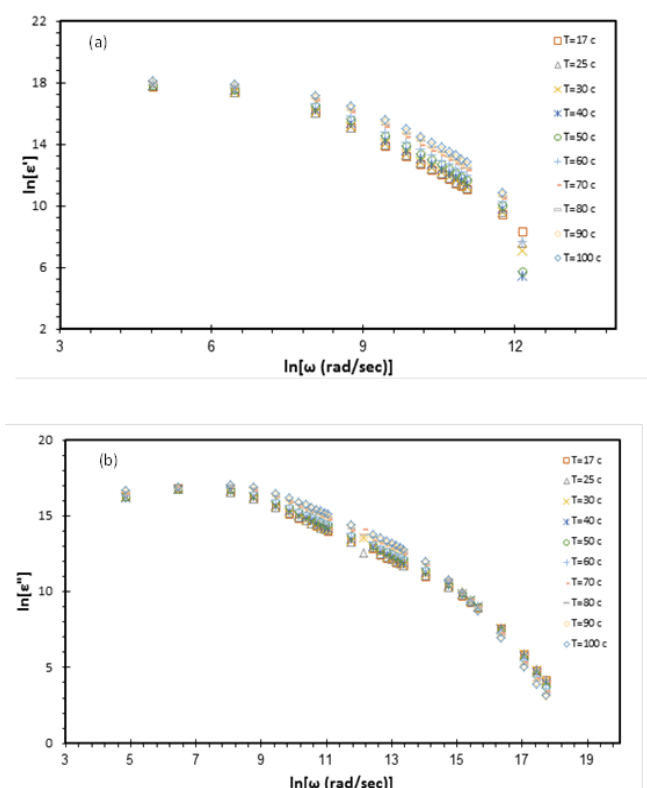


Fig. 8 The variation of a. Dielectric constant ϵ' , b. Dielectric loss ϵ'' with frequency of 0.22 M electrolyte at different temperatures.

same behavior is observed for plot of ϵ' and ϵ'' as a function of frequency at different temperatures for 0.22 M Mg(ClO₄)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 ϵ' and ϵ'' 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(ClO₄)₂ complex with Mg²⁺ ion intercalation cathodes, prototype tube cell was assembled using Mg ribbon anode and TiO₂ 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 $\sim 10 \mu\text{A}/\text{cm}^2$ 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 Mg²⁺ ions in the electrolyte into TiO₂ cathode. These results clearly suggest that DMTG/Mg(ClO₄)₂ complex based electrolyte

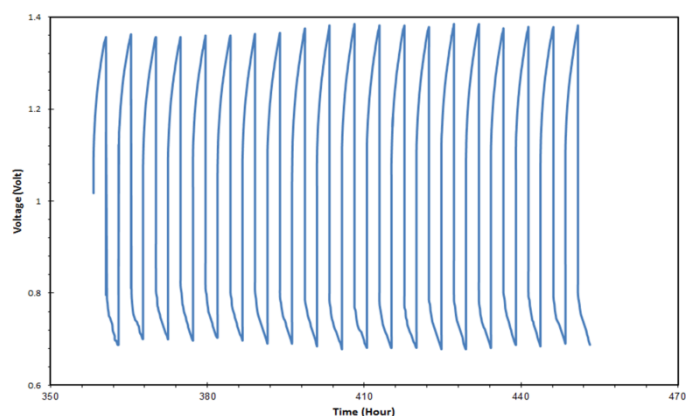


Fig. 9 Charge-discharge profiles of Mg/TiO₂ cell at charge/discharge time of 2/2 hours.

can be incorporated into rechargeable Mg batteries.

Fig. 10 a and b show the morphological effect of the electrochemical process on the surface of TiO₂ cathode. The relevant EDS spectrum was printed at the bottom of each image. Prior to the characterization, TiO₂ 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,

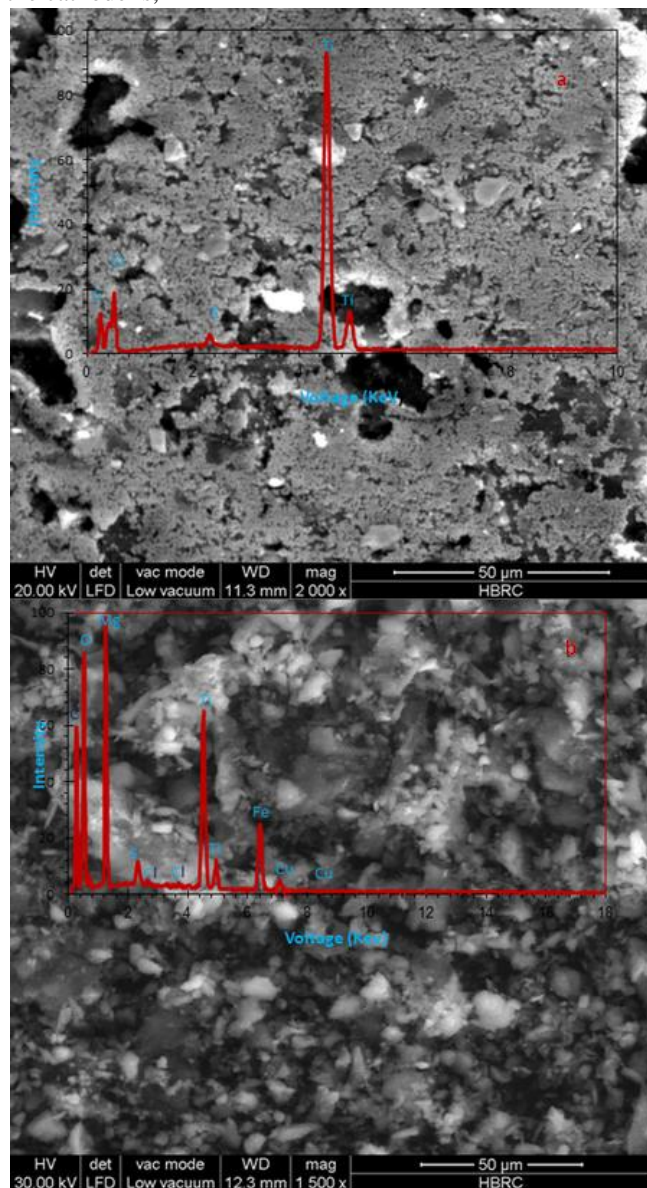
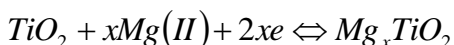


Fig. 10 EDS and SEM images of the TiO_2 cathode: (a) before cycling, (b) after cycling.



That is, during the first discharge, Mg^{2+} ion is inserted into TiO_2 structure from DMTG / $\text{Mg}(\text{ClO}_4)_2$ electrolyte, and desorbed from to electrolyte during the recharge.

4 CONCLUSION

In conclusion, DMTG / $\text{Mg}(\text{ClO}_4)_2$ 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.

5 ACKNOWLEDGMENTS

I'm grateful to the Science technology development fund of Egypt, grant number 4758.

The author thanks Prof. Sayed Badwy, Chemistry Department, Benha University for help in drawing chemical structure.

REFERENCES

- [1] Ju Q, Shi Y, Kan J. Performance study of magnesium-polyaniline rechargeable battery in 1-ethyl-3-methylimidazolium ethyl sulfate electrolyte. *Synthetic Metals* 2013;178:27– 33.
- [2] Liao C, Guo B, Jiang D, Custelcean R, Mahurin S, Sun X, Dai S, Highly Soluble Alkoxide Magnesium Salts for Rechargeable Magnesium Batteries, *J. Mater. Chem. A* 2014;2:581-584.
- [3] Huang Z, Masese T, Orikasa Y, Mori T, Minato T, Tassel C, Kobayashi Y, Kageyama H, Uchimoto Y, MgFePO_4F as a feasible cathode material for magnesium batteries. *J. Mater. Chem. A* 2014;2:11578-11582.
- [4] Benmayza A, Ramanathan M, Arthur T, Matsui M, Mizuno F, Guo J, Glans P, Prakash J, Effect of Electrolytic Properties of a Magnesium Organohaloaluminate Electrolyte on Magnesium Deposition. *J. Phys. Chem. C* 2013;117:26881–26888.
- [5] Jeremias S, Giffin G, Moretti A, Jeong S, Passerini S, Mechanisms of Magnesium Ion Transport in Pyrrolidinium Bis(trifluoromethanesulfonyl)imide-Based Ionic Liquid Electrolytes *J Phys Chem C*. 2014;118:28361.
- [6] Guo Y, Zhang F, Yang J, Wang F, Electrochemical performance of novel electrolyte solutions based on organoboron magnesium salts. *Electrochemistry Communications* 2012;18:24–27

- [7] Tuerxun F, Abulizi Y, NuLi Y, Su S, Yang J, Wang J, High concentration magnesium borohydride/tetraglyme electrolyte for rechargeable magnesium batteries. *Journal of Power Sources* 2015;276:255-261.
- [8] Su S, Huang Z, NuLi Y, Tuerxun F, Yang J, Wang J, A novel rechargeable battery with magnesium anode, titanium dioxide cathode, and magnesium borohydride/tetraglyme electrolyte. *Chem. Commun.* 2015;51:2641-2644
- [9] Sheha E, Ion transport properties of magnesium bromide/Dimethyl sulfoxide non-aqueous liquid electrolyte. *Journal of Advanced Research* (2015) xxx, xxx-xxx.
- [10] Mohtadi R, Mizuno F, Magnesium batteries: Current state of the art, issues and future perspectives. *Beilstein J. Nanotechnol.* 2014;5:1291-1311.
- [11] Cheng Y, Stolley R, Han K, Shao Y, Arey B, Washton N, et al, Highly active electrolytes for rechargeable Mg batteries based on a $[\text{Mg}_2(\mu\text{-Cl})_2]^{2+}$ cation complex in dimethoxyethane. *Phys. Chem. Chem. Phys.*, 2015;17:13307-13314.
- [12] Tutusaus O, Mohtadi R, Arthur T, Mizuno F, Nelson E, Sevryugina Y, An Efficient Halogen-Free Electrolyte for Use in Rechargeable Magnesium Batteries. *Angewandte Chemie* 54; 27:7900-7904.
- [13] Peng Z, Freunberger S, Chen Y, Bruce P. A reversible and higher-rate Li-O₂ battery. *Science* 2012;337:563.
- [14] Polu A, Kumar R, Mg²⁺-ion conducting poly(ethylene glycol)-TiO₂ composite polymer electrolytes for solid-state batteries. *Mater. Express* 2014;4:79-84.
- [15] Karlsson L, Mcgreedy R. Mechanisms of ionic conduction in Li₂SO₄ and LiNaSO₄: paddle wheel or percolation. *Solid State Ionics* 1995;76:301.
- [16] Ramesh S, Lu S, Morris E. Towards magnesium ion conducting poly(vinylidene-fluoride hexafluoropropylene)-based solid polymer electrolytes with great prospects: Ionic conductivity and dielectric behaviours. *J Taiwan Inst Chem E* 2012; 43:806.
- [17] Gondaliya N, Kanchan D, Sharma P, Jayswal M. Dielectric and Electric Properties of Plasticized PEO-AgCF₃SO₃-SiO₂ Nanocomposite Polymer Electrolyte System. *POLYMER COMPOSITES*—2012. DOI 10.1002/pc.22362.
- [18] Ahmad F, Sheha E. Preparation and physical properties of (PVA)_{0.7} (NaBr)_{0.3}(H₃PO₄)_{xM} solid acid membrane for phosphoric acid—Fuel cells. *J. Advanced Research* 2013;4:155-161.
- [19] Gershinsky G, Yoo H, Gofer Y, Aurbach D. Electrochemical and Spectroscopic Analysis of Mg²⁺ Intercalation into Thin Film Electrodes of Layered Oxides: V₂O₅ and MoO₃. *Langmuir* 2013;34:10964-10972.