

ORIGINAL ARTICLE

Ion transport properties of magnesium bromide/dimethyl sulfoxide non-aqueous liquid electrolyte



E. Sheha *

Physics Department, Faculty of Science, Benha University, Benha 13518, Egypt

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ABSTRACT

Nonaqueous liquid electrolyte system based dimethyl sulfoxide DMSO and magnesium bromide (MgBr_2) is synthesized via 'Solvent-in-Salt' method for the application in magnesium battery. Optimized composition of $\text{MgBr}_2/\text{DMSO}$ electrolyte exhibits high ionic conductivity of 10^{-2} S/cm at ambient temperature. This study discusses different concentrations from 0 to 5.4 M of magnesium salt, representing low, intermediate and high concentrations of magnesium salt which are examined in frequency dependence conductivity studies. The temperature dependent conductivity measurements have also been carried out to compute activation energy (E_a) by least square linear fitting of Arrhenius plot: ' $\log \sigma - 1/T$ '. The transport number of Mg^{2+} ion determined by means of a combination of d.c. and a.c. techniques is ~ 0.7 . A prototype cell was constructed using nonaqueous liquid electrolyte with Mg anode and graphite cathode. The Mg/graphite cell shows promising cycling.

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Introduction

Due to gasoline high cost and probability of oil depletion, demands for renewable energy sources increased. Rechargeable batteries are the most important sources of renewable energy especially batteries to run electric cars. But the dream of the spread of the electric car is still far because we need battery systems suitable for load leveling applications. They have to be large, safe, and made of cheap and abundant components.

Most importantly, it is mandatory that they have a very prolonged lifecycle [1,2].

The lithium (Li) battery used as a power source because of its high specific power and high energy density. However, high demand for Li battery tends to make increase in Li price due to geographically limitedness in the earth crust [1]. As an alternative to lithium, magnesium has been foregrounded. Magnesium batteries have recently attracted great interest due to their high energy density and environmentally friendly components, coupled with magnesium's low cost ($\sim \$2700/\text{ton}$ for Mg compared to $\$64,000/\text{ton}$ for Li) and abundance in the earth's crust ($\sim 13.9\%$ Mg compared to $\sim 0.0007\%$ of Li) [3–5].

The kinetically sluggish Mg intercalation and diffusion in cathode materials and the incompatibility between anode and electrolyte due to the high polarizing ability of the Mg^{2+} cation are the major obstacles that prohibit Mg batteries from

* Tel.: +20 1007414705.

E-mail address: ISLAM.SHIHAH@fsc.bu.edu.eg.

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commercialization [6–8]. Thus, the great challenge in the commercialization of Mg batteries is 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 [9].

The development of magnesium electrolytes is considered the most important challenge for the commercial application of rechargeable magnesium (Mg) batteries because electrolyte properties govern battery performance and determine the class of cathodes utilized [10]. Aurbach et al. [8] developed a prototype Mg cell using Mo_6S_8 Chevrel phase cathode, $\text{Mg}(\text{AlCl}_2\text{-EtBu})_2$ /tetrahydrofuran electrolyte with a little fade of capacity. However, the development of rechargeable Mg batteries still hindered by using electrolyte suffers 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 [11,12].

Magnesium bromide (MgBr_2) is the fast conducting salt in a number of crystalline and amorphous materials. 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. Recently, Peng et al. [13] report that a Li-O_2 cell composed of a DMSO-based electrolyte and a NPG electrode can sustain reversible cycling, retaining 95% of its capacity after 100 cycles and having >99% purity of Li_2O_2 formation at the cathode, even on the 100th cycle, and its complete oxidation on charge. Although, to date, there is no works on DMSO-based electrolyte for magnesium batteries have been done. This prompted us to try the test dimethyl sulfoxide/ MgBr_2 as an electrolyte for magnesium battery.

Upon the above considerations, a key obstacle to obtain the better performance, new electrolyte system for rechargeable magnesium batteries should be developed. Therefore, in this article, new classes of non-aqueous liquid ‘Solvent-in-Salt’ electrolytes, $\text{MgBr}_2/\text{DMSO}$ are discussed. The electrolytes were characterized by using XRD and impedance spectroscopy. Generally, this work mainly focuses on studies of ionic conductivity and Mg^{2+} ion transference with the aim of gaining understanding in ionic conduction of magnesium in this electrolyte system. With non-aqueous electrolyte optimum composition, Mg/Graphite cell is assembled, and its cycling performances will be briefly examined to evaluate the applicability of the electrolyte to solid-state magnesium batteries.

Experimental

All tested electrolytes consisted of a magnesium bromide (492 ppm of moisture, Sigma) with different concentrations, $x = 0.0, \dots, 0.55 \text{ M}$ in dimethyl sulfoxide (Loba Chemie). The resulting solutions were stirred for 2 h at room temperature.

The XRD patterns of MgBr_2 , $\text{MgBr}_2/\text{DMSO}$ precipitated solid product were taken using Rigaku diffractometer type RINT-Ultima IV/S. The diffraction system based with Cu tube anode with voltage 40 kV and current 40 mA.

Conductivity measurements of $\text{MgBr}_2/\text{DMSO}$ liquid electrolyte were performed using impedance method. Electrolyte

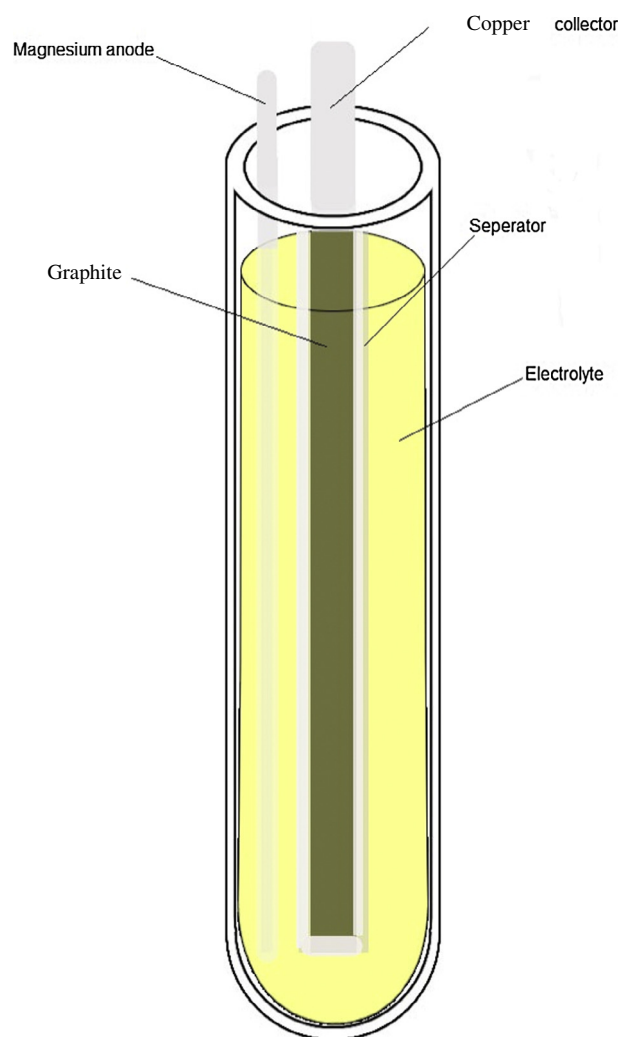


Fig. 1 Schematic design of the laboratory cell.

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.

Slurry was obtained by mixing 1 g graphite, 0.1 g magnesium sulfate and 0.2 g PVA binder using magnetic stirrer hot plate (60°C) for 2 h. The cathode (reduced electrode) is prepared by coating pole of stainless steel by 0.1 g of this slurry in dry atmosphere at 100°C for two hours. Entek PE membrane separator has been used. The whole assembly was shown in Fig. 1. The tube cell was discharged at room temperature on a multi-channel battery test system (NEWARE BTS-TC35) with the charge/discharge time of 2/2 h and 10 min rest. The current density was $10 \mu\text{A/cm}^2$.

Results and discussion

Plausible reaction model between MgBr_2 and DMSO is shown in Fig. 2a. In the hexahydrate ($\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$) the magnesium cation is surrounded only by water molecules, forming distinct octahedral [14]. By dissolving $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$ in DMSO two

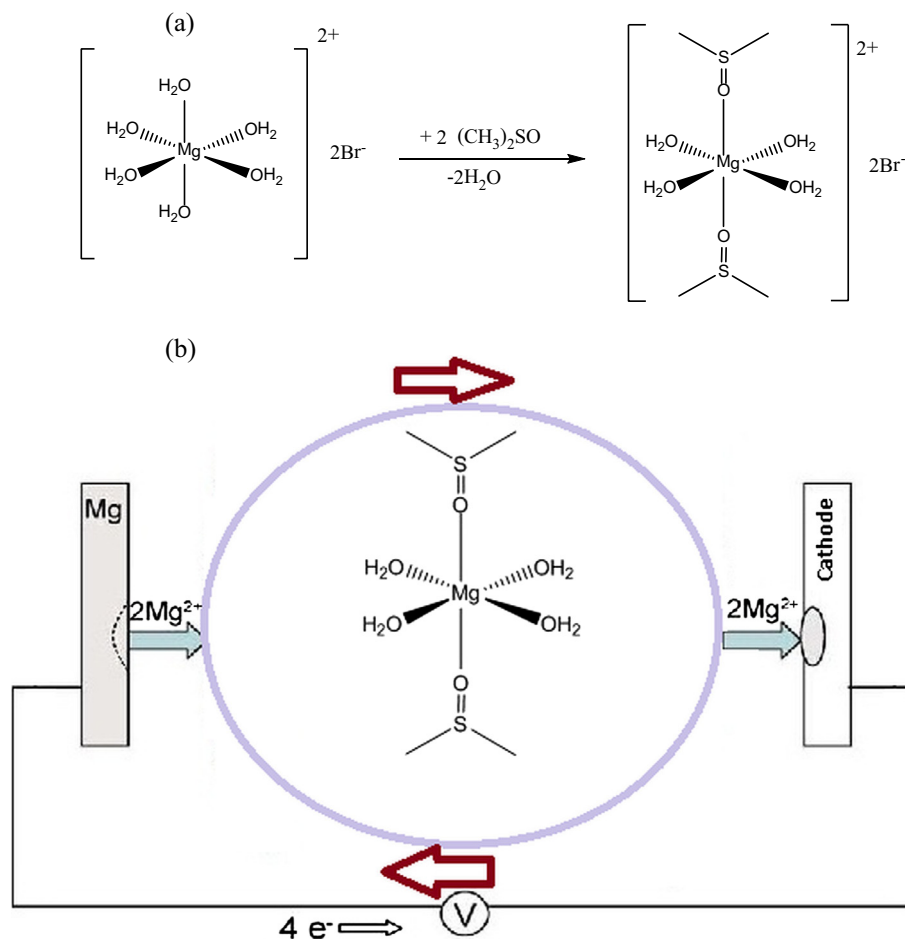


Fig. 2 (a) Proposed reaction scheme of DMSO/MgBr₂ electrolyte. (b) Expected schematic design of Mg²⁺ ion transport in Mg-cell.

water molecules are leaving the structure being replaced by DMSO molecules with Mg atom bridging two oxygen atoms. The magnesium-ion transference numbers were obtained by combining alternating-current (AC) impedance and direct-current (DC) polarization measurements using a symmetric Mg/electrolyte/Mg cell. First, AC impedance test was performed to obtain a total 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 $R_{DC} = V_{DC}/I_{DC}$) [15]. The transport

number of Mg²⁺ ion determined by means of a combination of d.c. and a.c. techniques is ~ 0.7 . The mechanism of ion transport likely proceeds via structure diffusion (exchange of the bridging (O–Mg–O)) or via vehicular transport (movement of the metal cations along with the first solvation shell) [16]. The prediction scheme of Mg²⁺ ion transports in operating Mg-cell is shown in Fig. 2b.

The reacting behavior of magnesium bromide and DMSO was studied by using XRD powder diffraction. Fig. 3 shows XRD pattern of pure MgBr₂ compound, and the MgBr₂/

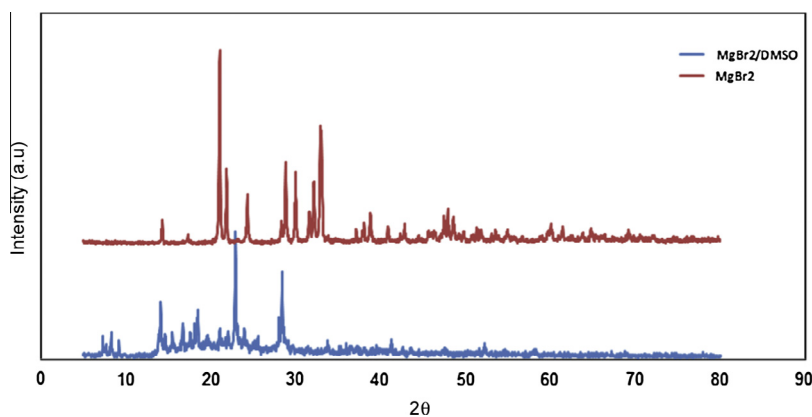


Fig. 3 XRD pattern of MgBr₂ and DMSO/MgBr₂ solid product.

DMSO solid product precipitated from super-saturated solution. It can be seen that there are significant differences between them. The intensity of the peaks decreased due to the reaction of MgBr_2 with DMSO. The data of pure MgBr_2 matched with JCPDS file No. 74-1040 for MgBr_2 hexahydrate with preferential orientation of the (111) direction, $2\theta = 22^\circ$

Table 1 XRD results of MgBr_2 and DMSO/ MgBr_2 solid product.

2Theta	FWHM (B)	d	Particle size (nm)
<i>Structure parameters of MgBr_2</i>			
21.05	0.12	4.21	67.30
32.94	0.12	2.71	69.00
33.06	0.12	2.70	69.02
28.82	0.12	3.09	68.32
29.98	0.18	2.97	45.67
21.86	0.15	4.06	53.91
<i>Structure parameters of $\text{MgBr}_2/\text{DMSO}$</i>			
22.91	0.12	3.87	67.52
28.40	0.12	3.13	68.26
14.12	0.09	6.26	88.91
18.47	0.12	4.79	67.04
28.05	0.09	3.17	90.94
16.72	0.15	5.29	53.51

((21) and (112) at $2\theta = 32.9^\circ$). XRD data of $\text{MgBr}_2/\text{DMSO}$ solid product precipitated from super-saturated solution exhibited low intensity peaks. New peaks are observed at $2\theta = 18^\circ$ and 22.2° . These peaks may be associated with structure perturbation due to the dehydration features [14], where two water molecules are leaving the structure being replaced by DMSO molecules with Mg atom bridging two oxygen atoms. Chemical reactivity between salt and solvent is a crucial issue. In fact, significant reactivity can induce the formation of new structure phases promote the ionic transfer.

The crystallite size D of pure MgBr_2 compound, and the $\text{MgBr}_2/\text{DMSO}$ solid product was calculated from X-ray data using Scherrer equation as given below [17]:

$$D = 0.9\lambda / (B \cdot \cos \theta) \quad (1)$$

where 0.9 is the Scherrer constant, λ is the wavelength of X-ray, B is the breadth of the pure diffraction profile and θ is the incidence angle of the X-ray. Using this formula, we have calculated the particle size of pure MgBr_2 compound, and the $\text{MgBr}_2/\text{DMSO}$ solid product in the range 50–70 nm as shown in Table 1.

Impedance spectroscopy is an excellent tool for characterizing many of the electrical properties of materials and their interfaces with electronically conducting electrodes. The frequency response analyses were carried out over a wide frequency range from 20 Hz to 10 MHz. Complex impedance plot

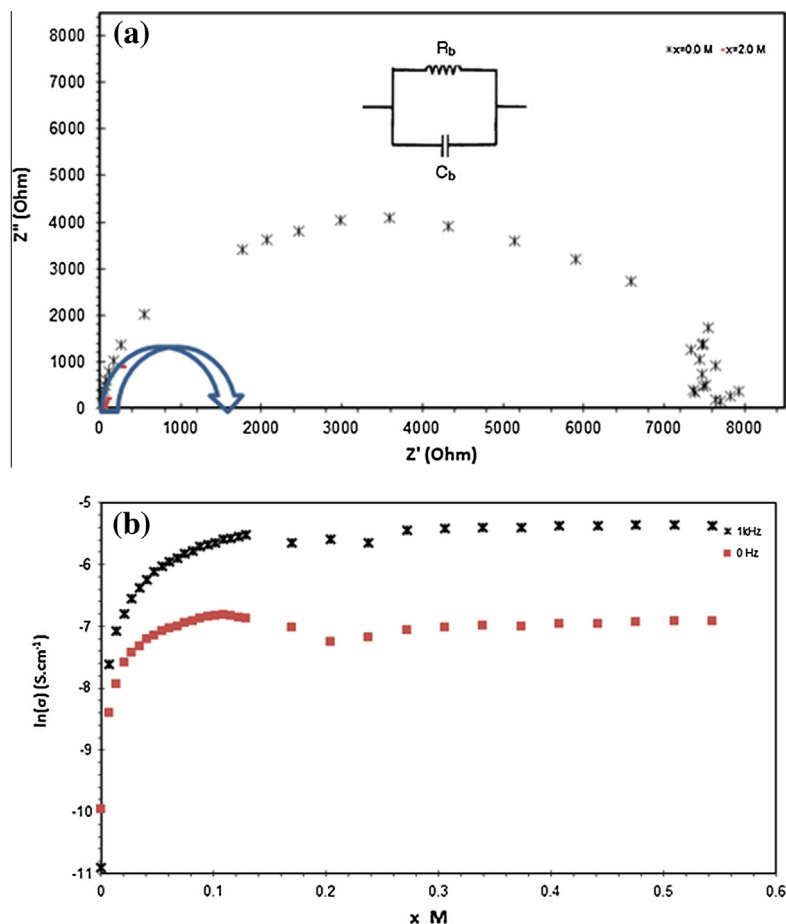


Fig. 4 (a) Cole–Cole plots of DMSO/ MgBr_2 electrolyte. (b) Variation of ionic conductivity of DMSO/ MgBr_2 electrolyte as a function of MgBr_2 concentration.

of $\text{MgBr}_2/\text{DMSO}$ electrolyte at different MgBr_2 concentrations and temperatures is shown in Fig. 4a. The complex plot shows semicircle which corresponds to the bulk resistance R_b with parallel combination of the frequency dependent capacitance C_g , Fig. 4a (inset). The diameter of the semicircle decreases with increasing concentrations and temperatures. 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 $\sigma_b = \frac{1}{R_b} \times \frac{L}{A}$, 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 $\text{MgBr}_2/\text{DMSO}$ electrolyte with respect to the content of MgBr_2 . The maximum conductivity of pure DMSO is found to be $\sim 10^{-6} \text{ S cm}^{-1}$ at room temperature ($\sim 25^\circ\text{C}$). A gradual increase in conductivity is observed, when the MgBr_2 salt is added in the DMSO and maximum conductivity around $\sim 10^{-4}$ – $10^{-2} \text{ S cm}^{-1}$ was achieved at $x = 0 > 0.16 \text{ M}$ of MgBr_2 for bulk and ac conductivity (1 kHz), respectively. On further addition of MgBr_2 a slight decrease in conductivity is observed, and the electrolyte is not dimensionally stable, showing glue like nature beyond the addition of 0.16 M of MgBr_2 . General expression of ionic conductivity is illustrated as below:

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

where n is the number of charge carriers, q is the charge of ions type, and μ is the mobility of ion pairs. Based on the equation above, the quantity and mobility of the charge carriers are the main factors that could affect the ionic conductivity. Therefore, the possible reason of enhancement in conductivity at low concentration of MgBr_2 is due to generation/introduction of mobile charged species, namely Mg^{2+} and Br^- . The decrease in conductivity, observed after $\sim 0.16 \text{ M}$ of MgBr_2 , is consistent with the higher viscosities of the more concentrated salt mixtures, and thus restricted free cation mobility (i.e., decrease of μ), as a result, lower ionic conductivity is observed [16,18,19].

Fig. 5a and b shows the frequency dependence of the total conductivity for $\text{MgBr}_2/\text{DMSO}$ electrolyte at different concentrations and temperatures, respectively. The conductivity of samples is found to increase with increasing frequency, as well as temperature. As compared to the high frequency region, the electrolyte shows a lower conductivity at low frequency. Slow periodic reversal of the applied electric field is the main contributor for this phenomenon. The low frequency dispersion region is due to the interfacial resistance or electrode polarization (EP). It refers to the electrodes being polarized as charge accumulates due to the slow periodic reversal of the electric field at low frequency. As the frequency decreases, more and

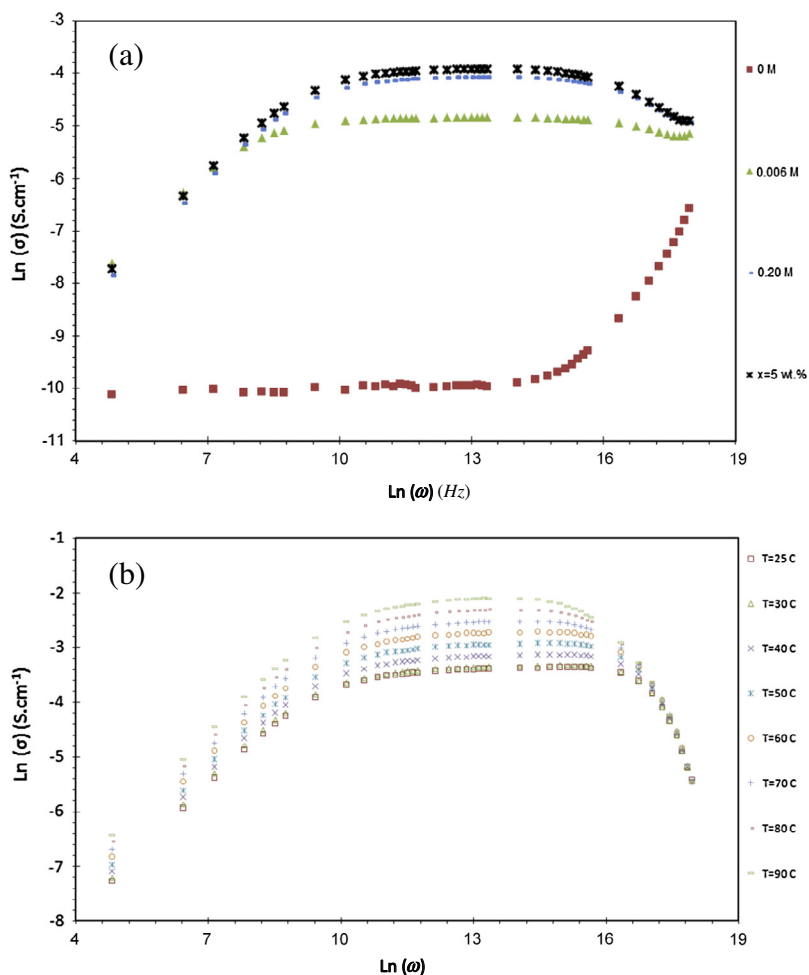


Fig. 5 (a) Frequency-conductivity dependence of DMSO/ MgBr_2 electrolyte at different MgBr_2 concentrations. (b) Frequency-conductivity dependence of DMSO/ MgBr_2 ($x = 0.4 \text{ M}$) electrolyte at different constant temperatures.

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 lower frequency. At higher frequency, the conductivity increases with frequency as the greater mobility of charge carriers and faster hopping of ions. As a result, the ion exchange process occurs effectively at higher frequency. An almost frequency-independent region is observed thereafter. It implies that the conductivity is equal to the bulk ionic conductivity. Above 1 MHz, the conductivity drops down (excluding pure DMSO) with the frequency. It is ascribed to the short period of the applied electric field for the charging to occur. The onset of conductivity drop decreases with increasing temperature. As the frequency increases, more and more (>1 MHz) charges return to accumulate at the electrodes and electrode interfaces due to ions not being able to follow the field variation at higher frequencies which leads to a decrease in the number of free mobile ions and eventually a drop in conductivity at higher frequency [20–22].

It can be noticed that the behavior follows universal power law [23]

$$\sigma_{ac}(\omega) = \sigma_{dc} + A\omega^{n_1} + A\omega^{n_2} \quad (3)$$

where σ_{dc} is the dc conductivity (the extrapolation of the plateau region to zero frequency), A is the frequency independent pre-exponential factor, ω is the angular frequency and n is the frequency exponent. The values of the exponent n have been obtained using the least square fitting of Eq. (3) for two regions are listed in Table 2. For the first region (20–800 Hz), the values of n_1 lie within the range of $0.4 < n < 0.8$. The values of n , predict the domination

of hopping conduction in MgBr₂/DMSO electrolyte. It can be noticed that the values of n for the second region (1 kHz–1 MHz) $n_2 \sim 0$, 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 ‘percolation’ model [24].

In the present study, the effects of temperature on the ionic conductivity of the selected electrolyte (0.4 M) were studied. The temperature dependence of dc conductivity (the extrapolation of the plateau region to zero frequency), and ac conductivity of MgBr₂/DMSO 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 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 regression values of all three chosen samples are near to unity, indicating that the temperature-dependent ionic conductivity for this system obeys Arrhenius rule. The results are tabulated in Table 2. The values of activation energy decrease with increasing frequency. This reflects the role of frequency to initiate ion transfer.

To further examine the usability of the electrolyte for a full cell with a magnesiation/de-magnesiation cathode, tube type cell using typical graphite cathode and Mg ribbon anode was assembled, and the charge–discharge properties were investigated at room temperature. Fig. 7 presents the typical potential time profile with the discharge and charge time limits of 2/2 h. The cell demonstrates reversible cycling behavior at

Table 2 Electrical parameters of DMSO/MgBr₂ ($x = 0.4$ M) electrolyte at room temperatures.

MgBr ₂ concentration $\times M$	Region 1 n_1	Region 2 n_2	Frequency ω (Hz)	Activation energy E (eV)
Conductivity–power exponent dependence			Frequency–activation energy dependence	
0	0.38	1.28	0	0.01
0.06	0.64	0.02	1 kHz	0.15
0.20	0.79	0.07	10 kHz	0.18
0.27	0.75	0.05	100 kHz	0.19
0.50	0.75	0.05	1 MHz	0.13
0.54	0.74	0.05	10 MHz	0.004

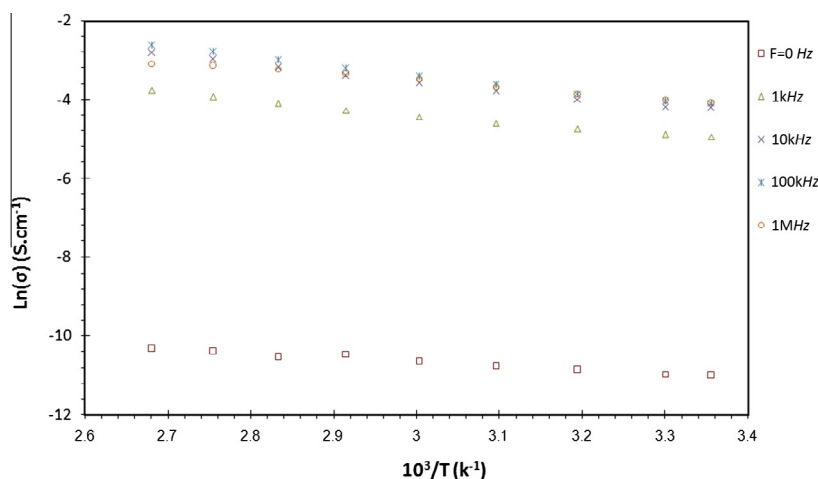


Fig. 6 Temperature–conductivity dependence of DMSO/MgBr₂ ($x = 0.4$ M) electrolyte at different constant frequencies.

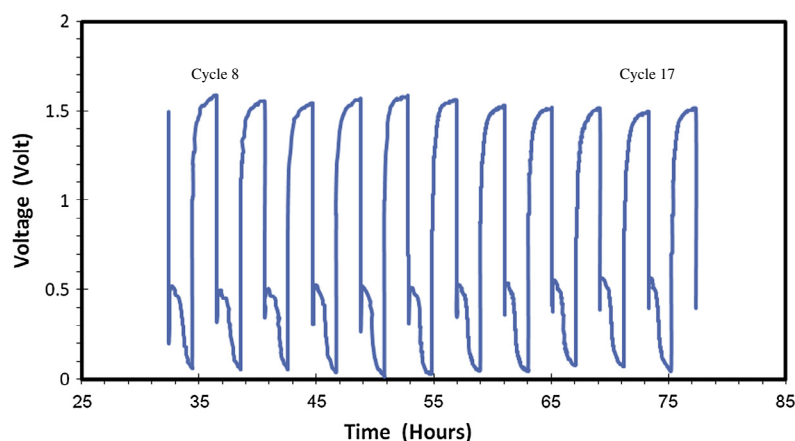
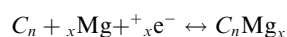


Fig. 7 Charge-discharge profiles of Mg/Graphite tube-cell at charge/discharge time of 2/2 h and 10 min rest.

current density $\sim 10 \mu\text{A}/\text{cm}^2$ with stable profile. The chemical reaction that probably takes place at the cathode is



That is, during the first discharge, Mg^{2+} ion is inserted into graphite structure from $\text{MgBr}_2/\text{DMSO}$ electrolyte, and deserted from graphite to electrolyte during the recharge.

Conclusions

Nonaqueous liquid electrolyte containing Mg^{2+} ions have been prepared and characterized by impedance techniques. Three different types of impedance spectra have been identified and differentiated by magnitude of ionic conductivity. Its trend increases almost proportional to the content of magnesium salt, and reaches highest ionic conductivity of $\sim 10^{-2} \text{ S}/\text{cm}$ at $> 0.16 \text{ M}$ of MgBr_2 salt. This can be related to the increase of charge carriers and amorphous phase from low to high level of dopant salt content. The Conductivity is found to be dependent on both temperature and frequency. From the results obtained, it can be observed that this non-aqueous liquid electrolyte system already shows great potential. It is worthy to be further investigated with incorporation of other additives, such as plasticizers, or ionic liquids. Nonaqueous liquid electrolyte system based dimethyl sulfoxide DMSO and magnesium bromide (MgBr_2), opens the door for the further development of electrolytes for the high energy magnesium batteries.

Conflict of interest

The author has declared no conflict of interest.

Compliance with Ethics Requirements

This article does not contain any studies with human or animal subjects.

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