



# Effect of Mg<sup>2+</sup> and Li<sup>+</sup> Concentration on Electrical Conductivity of Dimethyl Sulfoxide-Tetrahydrofuran Binary Mixture for Fabricating Mg and Li Based Energy Storage Devices

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## Authors' contributions

*This work was carried out in collaboration among all authors. Authors I-EMU and OC designed the study. Author EMF performed the experiment and wrote the first draft of the manuscript. Author OC vetted and modified the manuscript. All authors read and approved the final manuscript.*

## Article Information

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**Original Research Article**

**Received: 25/11/2022**

**Accepted: 15/01/2023**

**Published: 10/02/2023**

## ABSTRACT

**Aims:** The effect of magnesium (II) and lithium (I) ions concentration on mixed electrolyte of dimethylsulfoxide (DMSO) and tetrahydrofuran (THF) for the electrical conductivity of magnesium and lithium cells were studied.

**Methodology:** The DMSO-THF system was evaluated quantitatively with respect to conductivity, resistivity, and cell voltage at varying percentages of 100, 70, 50, 40, 30, 20, 10, 0 and at 25, 40, 50, 60 and 70°C using conductivity meter except for the cell voltages which was measured at 25°C using a digital multimeter.

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**Results:** The measured conductivities for the binary mixture showed higher values than the pure solvents. The mixing ratio of the DMSO-THF system for optimum battery performance with respect to resistivity, conductivity and electrochemical cell voltage was found to be between 50%-70% DMSO for  $\text{Li}^+$  ion concentration and 20%-70% DMSO for  $\text{Mg}^{2+}$  concentration. The result revealed greater tendency for redox reaction within the electrode-electrolyte region of  $\text{Mg}^{2+}$ -DMSO-THF.

**Conclusion:** This research has provided a new set of data on the parameters measured for battery fabrication with  $\text{Mg}^{2+}$  performing relatively better than  $\text{Li}^+$  in the mixed systems.

*Keywords: Electrolytes; cell voltage; thermodynamics; conductivity; mixing.*

## 1. INTRODUCTION

The expanding request for electrical vitality required to control the various viewpoints of the advanced human life led to a crucial center towards electricity energy storage systems or batteries [1,2,3]. Headways in energy storage innovations have proceeded to advance over time since its development. As one of the versatile battery frameworks, lithium-ion batteries have been at the cutting edge of incredible interests since the extraordinary discovery and brilliant utilization of Li-ion intercalation compounds as negative terminals [2]. Recently, magnesium has been at the receiving end of a grown consideration because it has higher energy capacities than lithium metal, i.e.,  $3832 \text{ mAhcm}^{-3}$  versus  $2061 \text{ mAhcm}^{-3}$  for lithium [4,5]. It may serve as a source of battery cost diminishments due to its common plenitude within the soil hull (5th most abundant element [6]). A study conducted recently by Yoshida et al. [7] has clearly shown that magnesium even in its solid-state possess the ability to display superionic conductivity of around  $10^{-3} \text{ Scm}^{-1}$  at ambient temperature.

The appropriateness of a solvent or solvent blend as an electrolyte requires the presence of a high dielectric constant and a reduced viscosity, which are seldom combined in a single solvent [8,9]. Binary mixtures are commonly utilized to make high conductivity electrolytes for batteries, with one component chosen for its low viscosity and the other for its high dielectric constant [10-13]. However, the chemistry of mixed organic solvents has provoked the interest of numerous researchers since these solvents have properties which will be more valuable than pure solvents in decreasing or eliminating high industrial contamination and natural destruction [11,14]. A few of the properties that can be utilized to characterize organic solvents incorporates conductivities, melting points,

boiling points, dielectric constant, density, flash point, resistivity, transport number, and solubility [10,15].

DMSO is a polar aprotic solvent, less toxic than other members of this class (such as dimethylformamide, dimethylacetamide), and is frequently used as a solvent for chemical reactions involving salts [16]. However, THF has been discovered to be recently used as co-solvent for lithium metal batteries, helping to stabilize the metal anode [17,18].

Measured conductivity is a good indicator of the presence or absence of conductive ions in solutions. The conductivity of a solution containing one electrolyte depends on the concentration of the electrolyte and temperature [15].

The limitations in the performance of the current state of the art battery systems as compared to the ever-increasing electricity storage demands of the modern times lead to alternative researches to enhance battery performance.

Dimethylsulfoxide is rarely used in preparing mixed solvents for electrolyte purposes in battery cells; a positive result from this work will raise its bar to an important niche position in the market for electricity storage systems.

In light of the above properties for effective and efficient battery functionality, it is imperative to evaluate the thermodynamic properties of mixed solvent media.

Therefore, this study evaluates the performance properties with respect to conductivity, cell voltage, and Gibbs free energy of mixed electrolyte of dimethylsulfoxide (DMSO) and tetrahydrofuran (THF) for magnesium and lithium cells.

## 2. MATERIALS AND METHODS

### 2.1 Materials

The dimethylsulfoxide (DMSO, Sigma-Aldrich, 99.50%), tetrahydrofuran (THF, Sigma-Aldrich, 99.50%), magnesium sulphate ( $\text{MgSO}_4$ , Sigma-Aldrich, 99.95%), and lithium sulphate ( $\text{Li}_2\text{SO}_4$ , Sigma-Aldrich, 99.95%) were all commercially obtained.

### 2.2 Sample Preparation

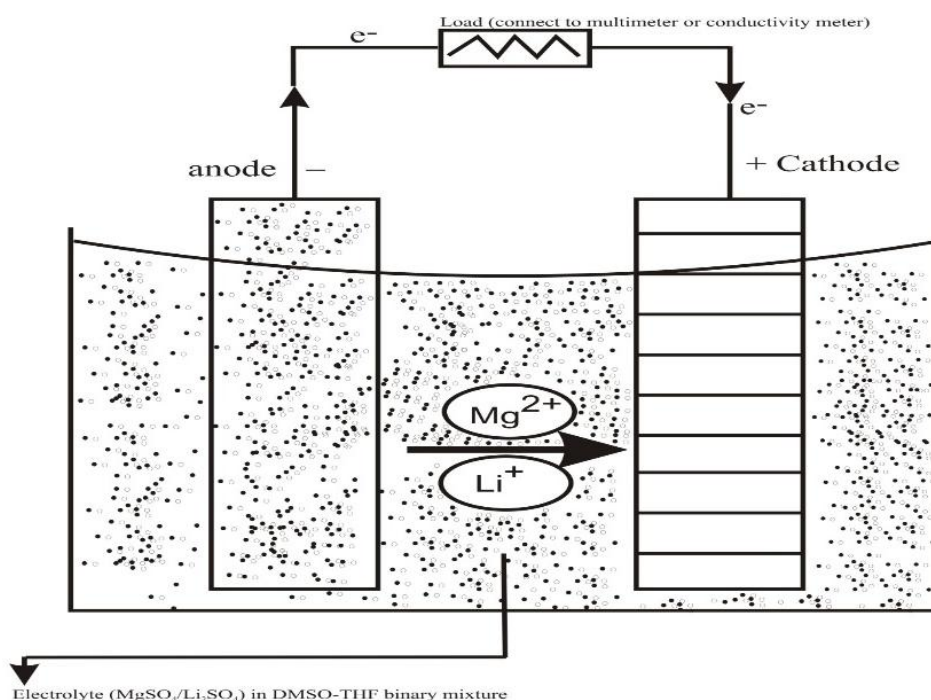
The binary mixtures of DMSO/THF were prepared in various percentages of 100, 70, 50, 40, 30, 20, 10 and 0%, which corresponds to mole fractions of 1.00, 0.70, 0.50, 0.40, 0.30,

0.20, 0.10 and 0.00 (Table 1). The working temperatures were 25, 40, 50, 60 and 70°C. Different concentrations of 0.1, 0.5 and 1.0 M of  $\text{MgSO}_4$  and  $\text{Li}_2\text{SO}_4$  were prepared in various DMSO-THF solvent percentages by dissolving 0.60, 3.01 and 6.02 g of  $\text{MgSO}_4$ , as well as 0.55, 2.75 and 5.50 g of  $\text{Li}_2\text{SO}_4$  respectively in 50 mL of the binary solvent. The weighing of the electrolytes was carried out on an electronic weighing scale (model no: ATX124) with a precision of  $\pm 0.001$  g. At the different concentrations of the binary mixture, the conductivities and resistivities were measured using a conductivity meter, and the electrochemical cell voltage were measured at the same different concentrations using a digital multimeter as shown in Fig. 1.

**Table 1. Mole fractions of DMSO/THF system**

% DMSO	$X_1$	$X_2$
100	1.00	0.00
70	0.70	0.30
50	0.50	0.50
40	0.40	0.60
30	0.30	0.70
20	0.20	0.80
10	0.10	0.90
0	0.00	1.00

Where,  $X_1$  = Mole fraction of DMSO in the system;  $X_2$  = Mole fraction of THF in the system



**Fig. 1. Electrochemical set-up**

### 3. RESULTS AND DISCUSSION

#### 3.1 Conductivity

The concentration of the ionic species in a solution is a determinant factor in the conductivity behavior of the solution. The measured conductivity values for both  $\text{Li}_2\text{SO}_4$  and  $\text{MgSO}_4$  electrolytes in the DMSO-THF binary system (Figs. 2-7) showed an increase in the conductivity values for the various concentrations in the DMSO-THF system as the percentage composition of DMSO in the mixture increased [9]. This varying conductivity values were attributed to the changes in ion mobility in the system, as a result of the changes in concentrations and temperatures of the system [19]. Tobishima et al. [20] reported that the high molar conductivity of

pure THF is attributed to the low viscosity of the solvent.

The result of this study reveals that maximum conductivity was obtained at 70% DMSO in 1.0 M  $\text{MgSO}_4$  in the DMSO-THF system at 70°C.

The result further revealed that conductivity increased in all the concentrations of the electrolytes as temperatures increased from 40-70°C.

Matsuda et al. [21] reported that such results showed that solvent-solvent and ion-solvent interactions enhancement due to increase in temperature contributed to the improvement of conductance. This net ion conductivity increment could be attributed to the varying properties of the solvents mixed.

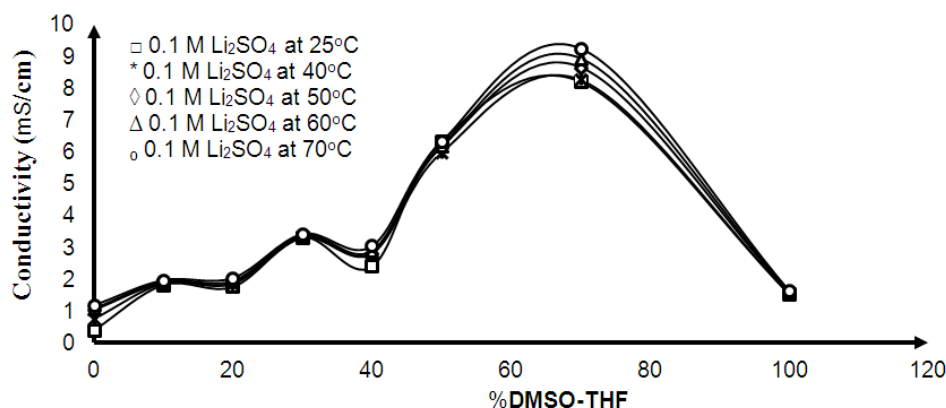


Fig. 2. Conductivity of 0.1M  $\text{Li}_2\text{SO}_4$  with various %DMSO-THF mixtures at 25-70°C

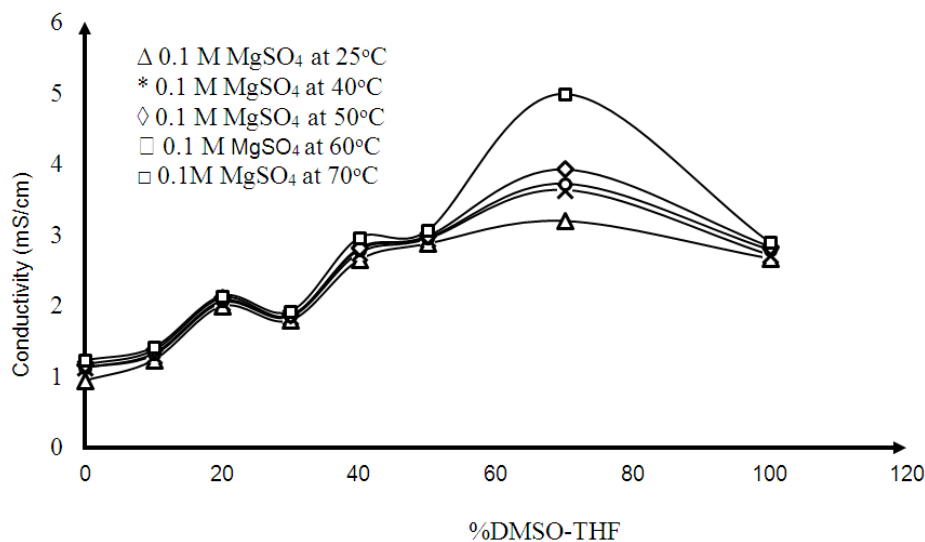


Fig. 3. Conductivity of 0.1M  $\text{MgSO}_4$  with various %DMSO-THF mixtures at 25-70°C

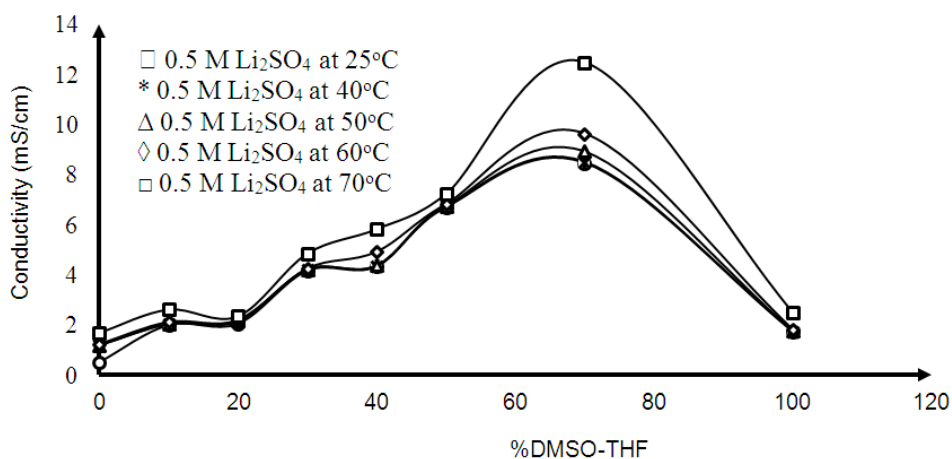


Fig. 4. Conductivity of 0.5M  $\text{Li}_2\text{SO}_4$  with various %DMSO-THF mixtures at 25-70°C

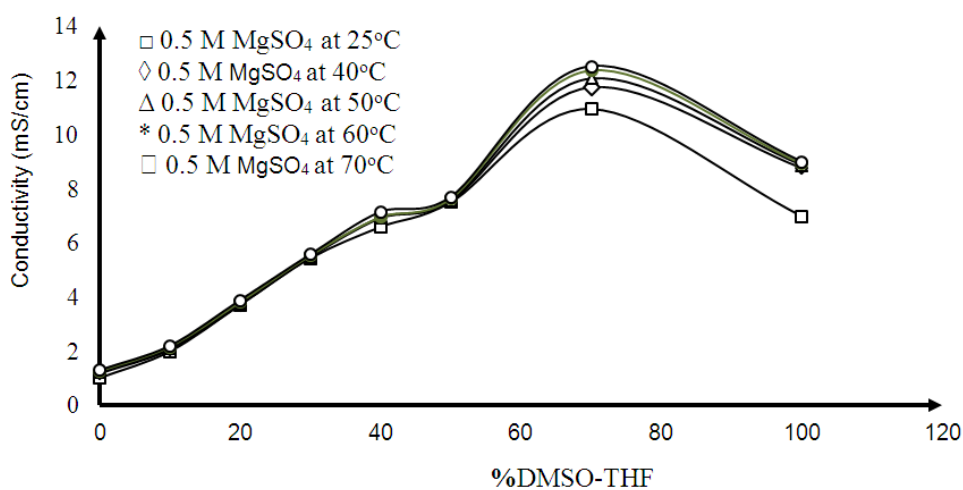


Fig. 5. Conductivity of 0.5M  $\text{MgSO}_4$  with various %DMSO-THF mixtures at 25-70°C

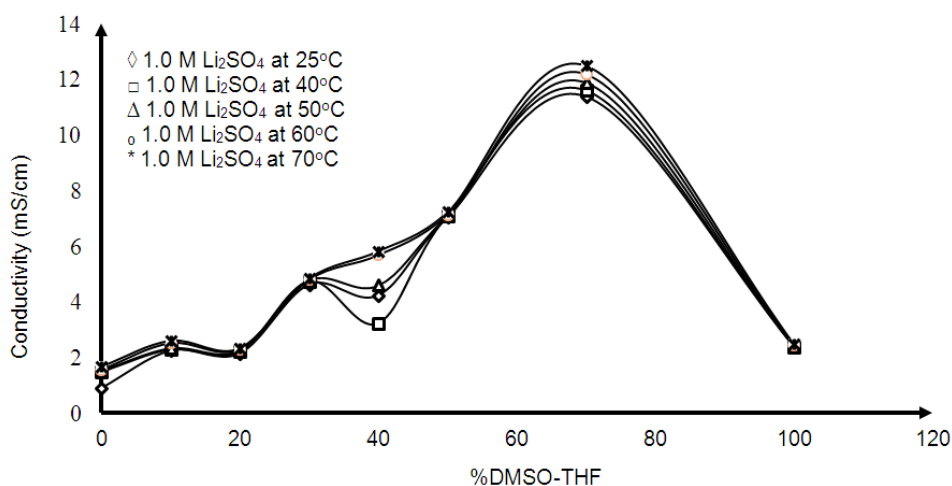
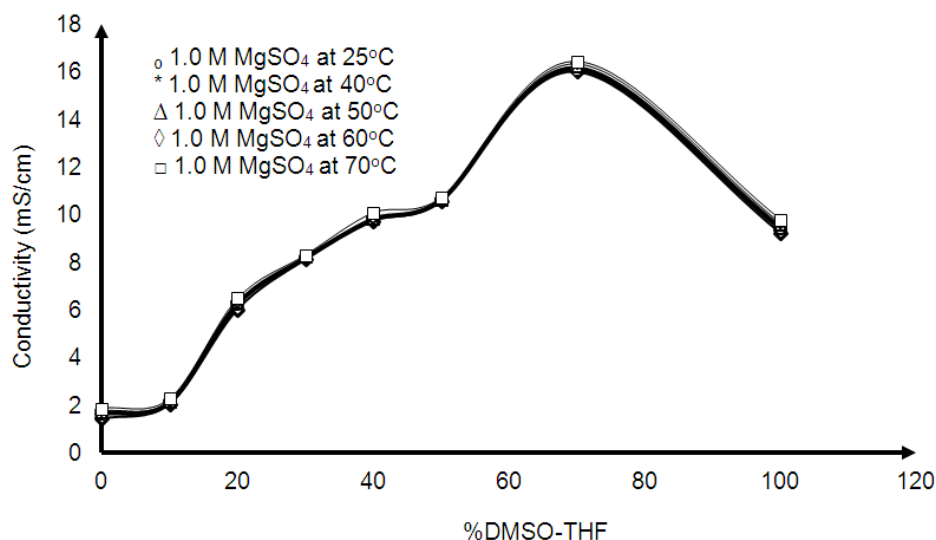


Fig. 6. Conductivity of 1.0M  $\text{Li}_2\text{SO}_4$  with various % DMSO-THF mixtures at 25-70°C



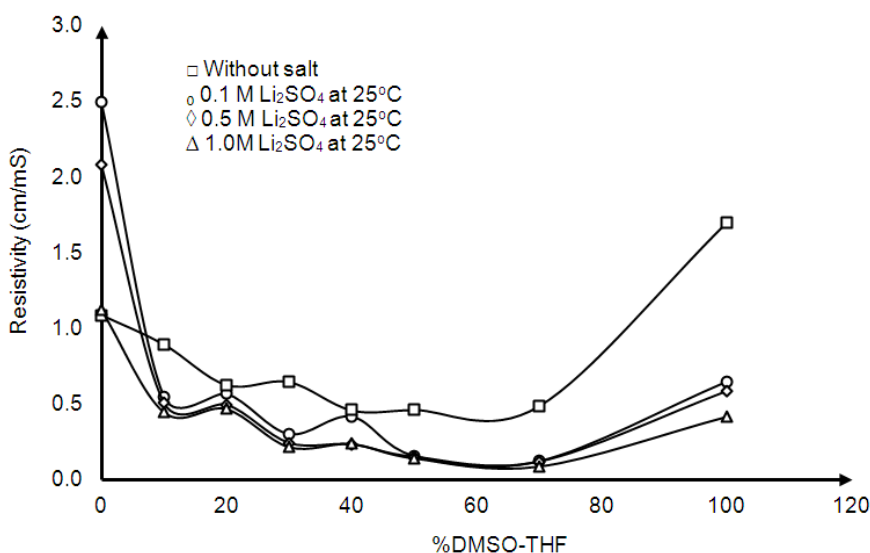
**Fig. 7. Conductivity of 1.0M MgSO<sub>4</sub> with various %DMSO-THF mixtures at 25-70°C**

Comparing the conductivity results obtained in DMSO-THF system containing 1.0 M of Li<sub>2</sub>SO<sub>4</sub> and 1.0 M of MgSO<sub>4</sub>, the system containing MgSO<sub>4</sub> gave the highest conductivity relative to the Li<sub>2</sub>SO<sub>4</sub> system. This can be attributed to the differences in their electronic charge i.e., Mg<sup>2+</sup> being greater than Li<sup>+</sup> as they moved through the solution (Ibezim-Ezeani et al. [22]).

However, as the concentrations of Li<sub>2</sub>SO<sub>4</sub> and MgSO<sub>4</sub> increased in the DMSO-THF system, the conductivity values increased [22]. The electrolyte solution containing MgSO<sub>4</sub> yields better conductivity than that containing Li<sub>2</sub>SO<sub>4</sub> at high concentrations.

### 3.2 Resistivity

The result revealed that minimum resistivity value was obtained at 70% DMSO with 1.0 M MgSO<sub>4</sub> (Fig. 11) in the DMSO-THF system at 25°C. The minimum resistivity was disrupted above 70% DMSO composition in all the concentrations of the Mg<sup>2+</sup> and Li<sup>+</sup> ions (Figs. 8-11). The measure of the resisting power of a specified material to the flow of an electric current is the resistivity of that material. Hence, the lower the resistivity of the material, the higher its conductivity. Therefore, mg<sup>2+</sup> ion showed higher conductivity than the Li<sup>+</sup> ion.



**Fig. 8. Resistivity of Li<sub>2</sub>SO<sub>4</sub> concentrations in %DMSO-THF mixtures at 25°C**

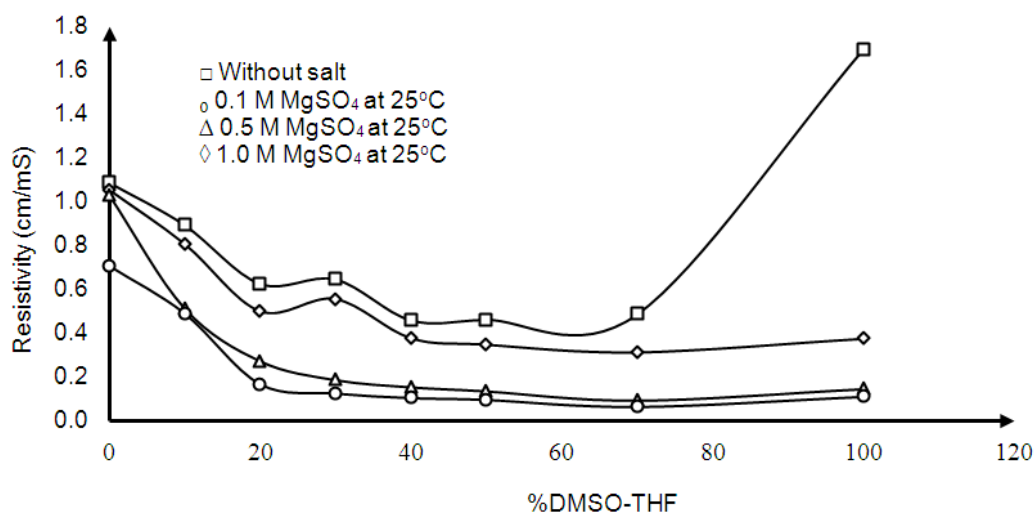


Fig. 9. Resistivity of  $\text{MgSO}_4$  concentrations in %DMSO-THF mixtures at  $25^\circ\text{C}$

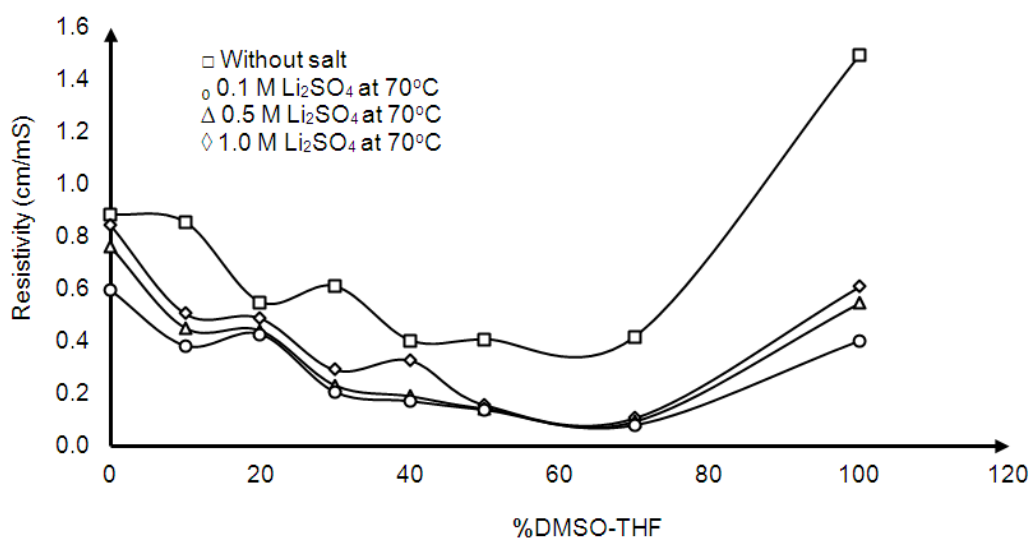


Fig. 10. Resistivity of  $\text{Li}_2\text{SO}_4$  concentrations in various %DMSO-THF mixtures at  $70^\circ\text{C}$

### 3.3 Electrochemical Cell Voltage

The measured electrochemical cell voltage of  $\text{Li}_2\text{SO}_4$ -DMSO-THF system at  $25^\circ\text{C}$  (Table 2) showed maximum cell voltage at 50% DMSO-THF in 0.1 M  $\text{Li}_2\text{SO}_4$  while the measured electrochemical cell voltage of  $\text{MgSO}_4$ -DMSO-THF system at  $25^\circ\text{C}$  (Table 3) showed maximum cell voltage at 20% DMSO-THF in 1.0 M  $\text{MgSO}_4$ . The measured electrochemical cell voltage of the system revealed optimum value at 20% DMSO-THF with 1.0 M  $\text{Mg}^{2+}$  ion. In 2000, Anusiem postulated that cell voltage in concentration cells is dependent on the difference in concentration of ions in the cells [23].

### 3.4 Gibbs Free Energy

The deduced values of Gibbs free energy change ( $-\Delta G$ ) for  $\text{Li}_2\text{SO}_4$ -DMSO-THF and  $\text{MgSO}_4$ -DMSO-THF systems respectively was obtained from the expression in equation 1.

$$-\Delta G = nFE^\circ \quad (1)$$

Where,

$n$  = Number of moles of electrons transferred (1 and 2 for  $\text{Li}^+$  and  $\text{Mg}^{2+}$  respectively)  
 $F$  = Faraday's constant ( $\approx 96500 \text{ Cmol}^{-1}$ ),  $E_{\text{cell}}$   
 = Measured cell voltage.



The results in Tables 2 and 3 revealed higher negative  $\Delta G$  values for  $MgSO_4$ -DMSO-THF system than  $Li_2SO_4$ -DMSO-THF system, which suggest greater tendency (spontaneity) for redox reaction within the

electrode-electrolyte compartment to produce higher potential difference [24]. This result is an improvement on the stability and safety performance using DMSO-THF binary mixture.

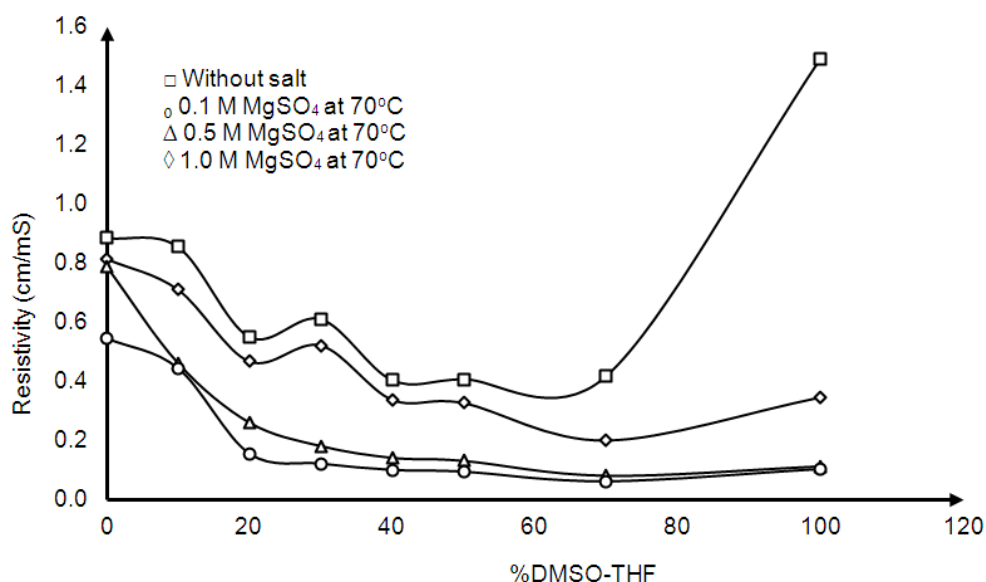


Fig. 11. Resistivity of  $MgSO_4$  concentrations in various %DMSO-THF mixtures at  $70^\circ C$

Table 2. Cell voltage and free energy for DMSO-THF system with various concentrations of  $Li^+$  at  $25^\circ C$

% DMSO	Without ion		With 0.1 M		With 0.5 M		With 1.0 M	
	$E_{cell}$ (V)	$-\Delta G$ (kJ)	$E_{cell}$ (V)	$-\Delta G$ (kJ)	$E_{cell}$ (V)	$-\Delta G$ (kJ)	$E_{cell}$ (V)	$-\Delta G$ (kJ)
100	0.137	13.221	0.141	13.607	0.147	14.186	0.085	8.203
70	0.130	12.545	0.134	12.931	0.137	13.221	0.140	13.510
50	0.140	13.510	0.143	13.800	0.132	12.738	0.120	11.580
40	0.147	14.186	0.096	9.264	0.030	2.895	0.085	8.203
30	0.065	6.272	0.105	10.133	0.098	9.457	0.052	5.018
20	0.139	13.413	0.074	7.141	0.082	7.913	0.091	8.782
10	0.102	9.843	0.059	5.694	0.051	4.922	0.031	2.992
0	0.020	1.930	0.012	1.158	0.036	3.474	0.021	2.027

Table 3. Cell voltage and free energy for DMSO-THF system with various concentrations of  $Mg^{2+}$  at  $25^\circ C$

% DMSO	Without ion		With 0.1 M		With 0.5 M		With 1.0 M	
	$E_{cell}$ (V)	$-\Delta G$ (kJ)	$E_{cell}$ (V)	$-\Delta G$ (kJ)	$E_{cell}$ (V)	$-\Delta G$ (kJ)	$E_{cell}$ (V)	$-\Delta G$ (kJ)
100	0.137	26.441	0.080	15.440	0.127	24.511	0.141	27.213
70	0.130	25.090	0.112	21.616	0.083	16.019	0.092	17.756
50	0.140	27.020	0.082	15.826	0.120	23.160	0.105	20.265
40	0.147	28.371	0.072	13.896	0.065	12.545	0.091	17.563
30	0.065	12.545	0.082	15.826	0.132	25.476	0.138	26.634
20	0.139	26.827	0.072	13.896	0.095	18.335	0.170	32.810
10	0.102	19.686	0.069	13.317	0.039	7.527	0.050	9.650
0	0.020	3.860	0.010	1.930	0.026	5.018	0.030	5.790



#### 4. CONCLUSION

Significant information regarding the mixing behavior of DMSO-THF have been provided from the results of experimental measurements. The results indicated that DMSO-THF solvent mixture showed higher conductivities and electrochemical cell voltage in magnesium battery system than in lithium battery system, and at increased percentage of DMSO-THF in the system. The mixing ratio of the DMSO-THF system for optimum battery performance with respect to resistivity, conductivity and electrochemical cell voltage was found to be between 50%-70% DMSO for  $\text{Li}^+$  ion and 20%-70% DMSO for  $\text{Mg}^{2+}$  ion. This study showed that the mixing of organic solvents improved the performance behavior, thereby making them suitable for use as electrolytes in lithium and magnesium cells. This study recommends that the art of mixing electrolytes be employed in the construction of battery cells in order to improve the performance of the battery, thereby bridging the gap between the ever-increasing demand for electricity storage and the performance of batteries.

#### COMPETING INTERESTS

Authors have declared that no competing interests exist.

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DOI: 10.1039/D0CP02609C

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