Original Research Article

Correlation of Mg^{2+} And Li^{+} Salts on the Conductance of Dimethyl Sulfoxide-Tetrahydrofuran Binary Mixture for Magnesium and Lithium Cells

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ABSTRACT

Aims The effect of magnesium and lithium salts on mixed electrolyte of dimethylsulfoxide (DMSO) and tetrahydrofuran (THF) for magnesium and lithium cells were studied.

Methodology: The DMSO-THF system was quantitatively studied at varying percentages of 100, 70, 50, 40, 30, 20, 10 and 0% of DMSO, as well as the conductivity of 0.1, 0.5 and 1.0 M concentrations of lithium sulphate (Li_2SO_4) and magnesium sulphate ($MgSO_4$) salt solutions of the binary systems at 25, 40, 50, 60 and 70^{o}C. The resistivity and conductivity values of the binary systems were measured at different concentrations and temperatures using conductivity meter. The cell voltages, from which free energy was evaluated, were measured at 25^{o}C using a digital multimeter.

Results: The measured conductivities for mixed solvents 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 Li_2SO_4 salt and 30%-70% DMSO for $MgSO_4$ salt. The result revealed greater tendency for redox reaction within the electrode-electrolyte region of $MgSO_4$-DMSO-THF.

Conclusion: This research has provided a new set of data on the parameters measured with $MgSO_4$ performing relatively better than Li_2SO_4 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 $mAhcm^{-3}$ versus 2061 $mAhcm^{-3}$ 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} 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. MATERIAL AND METHODS

2.1 Materials

The solvents, dimethylsulfoxide (DMSO, Sigma-Aldrich, 99.50%) and tetrahydrofuran (THF, Sigma-Aldrich, 99.50%), and the salts, magnesium sulphate ($MgSO_4$, Sigma-Aldrich, 99.95%) and lithium sulphate (Li_2SO_4, Sigma-Aldrich, 99.95%) were all commercially obtained.

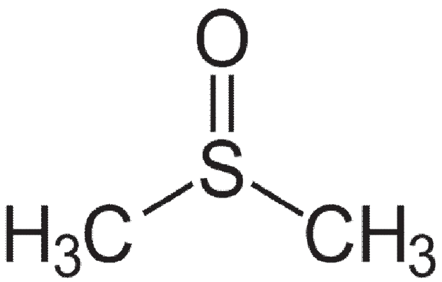

Figure 1: Structural formula of Dimethylsulfoxide

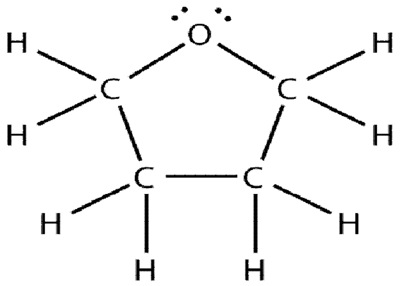

Figure 2: Structural formula of Tetrahydrofuran

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% of DMSO, which corresponds to mole fractions of 1.00, 0.70, 0.50, 0.40, 0.30, 0.20, 0.10 and 0.00 of % DMSO for DMSO/THF system respectively (Table 1). The working temperatures were 25, 40, 50, 60 and 70ºC. Different concentrations of 0.1, 0.5 and 1.0 M of $MgSO_4$ and Li_2SO_4 were prepared in various DMSO-THF solvent percentages by dissolving 0.60, 3.01 and 6.02 g of $MgSO_4$, as well as 0.55, 2.75 and 5.50 g of Li_2SO_4 respectively in 50 mL of the binary solvent. The weighing of the salts was carried out on an electronic weighing scale (model no: ATX124) with a precision of ± 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 voltages were measured at the same different concentrations using a digital multimeter.

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.

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 Li_2SO_4 and $MgSO_4$ salts in the DMSO-THF binary system (Figures 3-8) showed an increase in the conductivity values for the various concentrations for both Li_2SO_4 and $MgSO_4$ salts in the DMSO-THF system as the percentage composition of DMSO in the mixtures increased [9]. This varying conductivity values are 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.

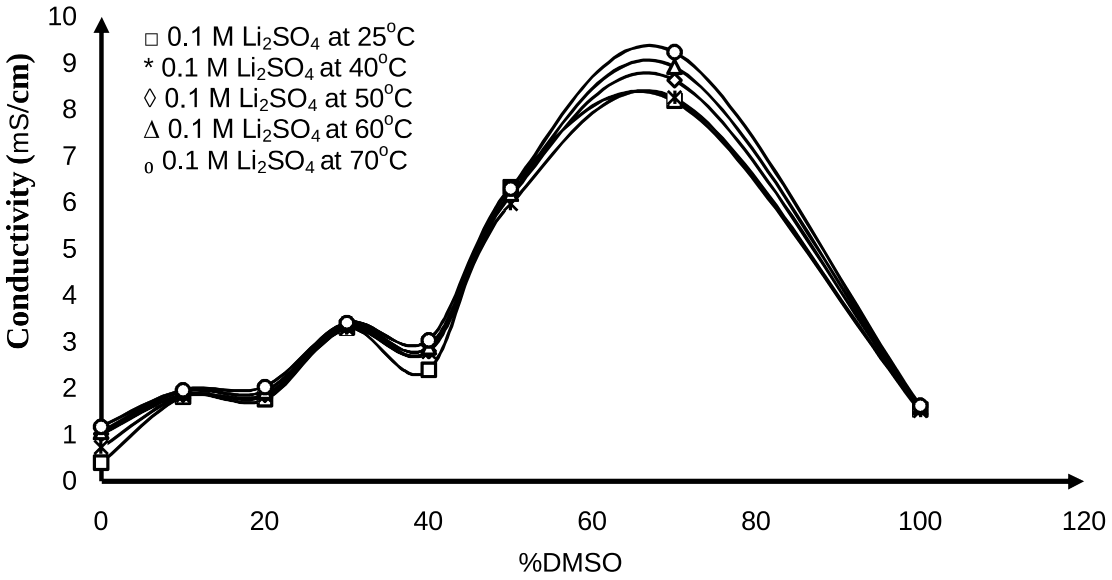

Fig. 3. Conductivity of 0.1M Li_2SO_4 with various %DMSO-THF mixtures at 25-70^oC

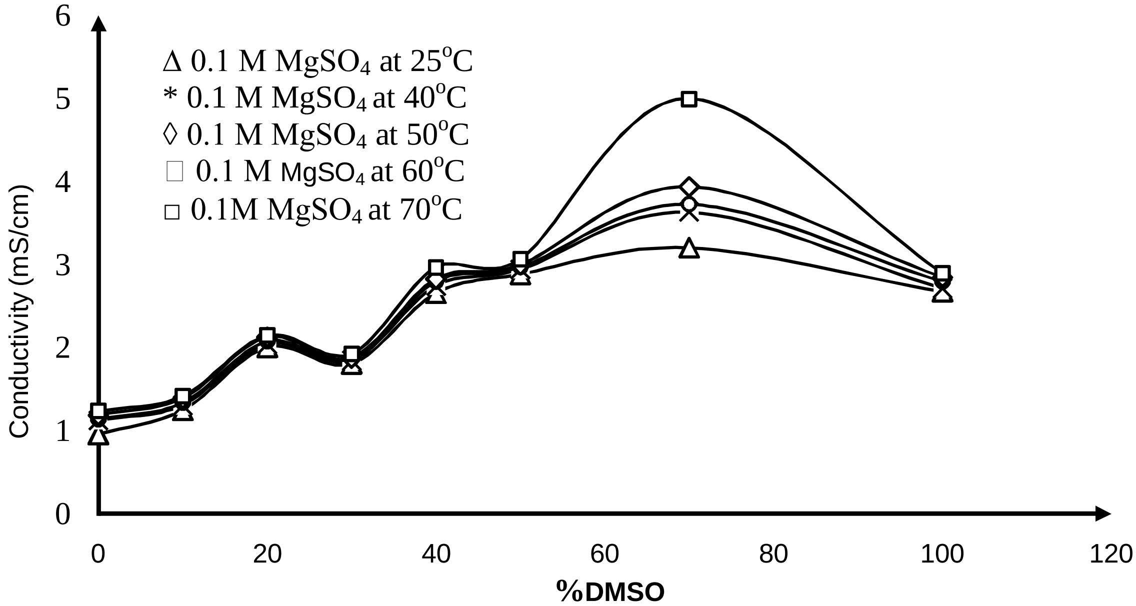

Fig. 4. Conductivity of 0.1M $MgSO_4$ with various %DMSO-THF mixtures at 25-70°C

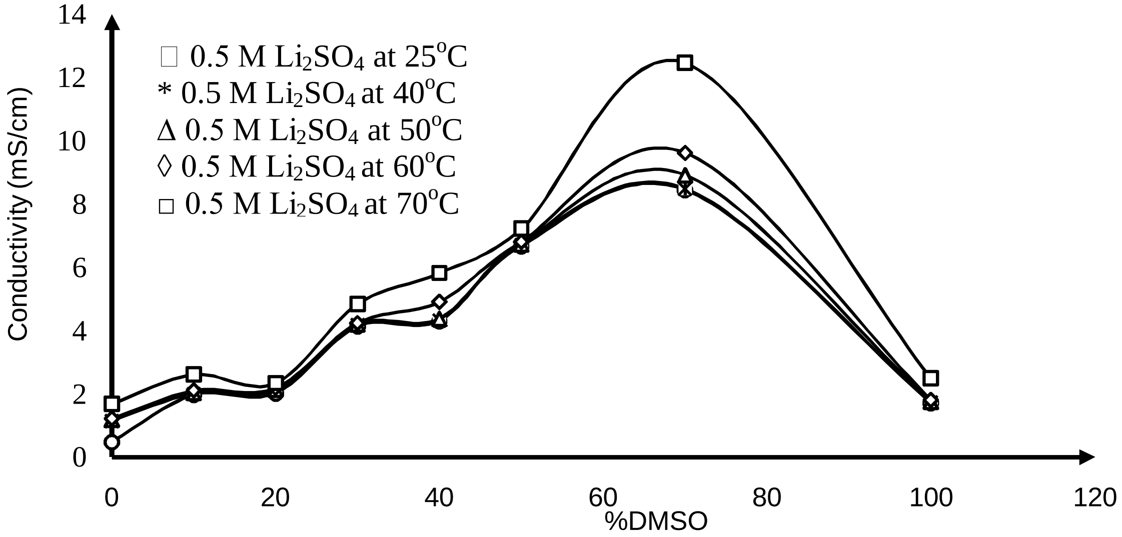

Fig. 5. Conductivity of 0.5M Li_2SO_4 with various %DMSO-THF mixtures at 25-70°C

For the DMSO-THF system containing Li_2SO_4 salt, maximum conductivity was obtained at 40% DMSO without salt, 70% DMSO in 0.1 M Li_2SO_4, 70% DMSO in 0.5 M Li_2SO_4 and 70% DMSO in 1.0 M Li_2SO_4 in the DMSO-THF system respectively at 25°C.

On the other hand, for the DMSO-THF system containing $MgSO_4$ salt, maximum conductivity was obtained at 70% DMSO in 0.1 M $MgSO_4$, 70% DMSO in 0.5 M $MgSO_4$ and 70% DMSO in 1.0 M $MgSO_4$ in the DMSO-THF system respectively at 25°C.

The result further revealed that at increased temperatures of 40, 50, 60 and 70°C; the maximum conductivity was obtained at 70% DMSO-THF in 0.1, 0.5 and 1.0 M Li_2SO_4 and $MgSO_4$ in the DMSO-THF system respectively. 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.

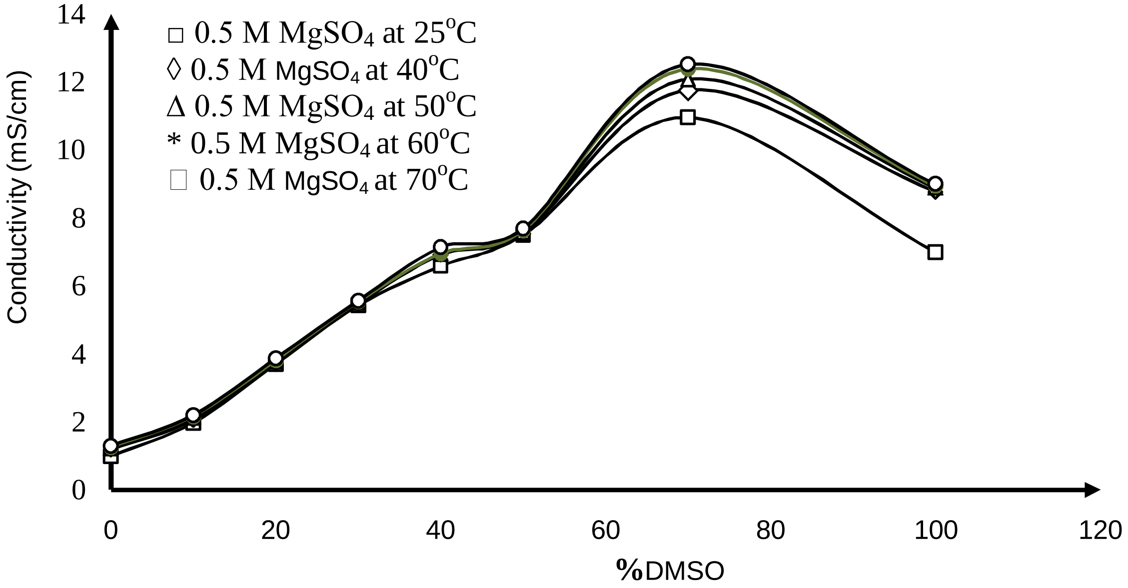

Fig. 6. Conductivity of 0.5M $MgSO_4$ with various %DMSO-THF mixtures at 25-70°C

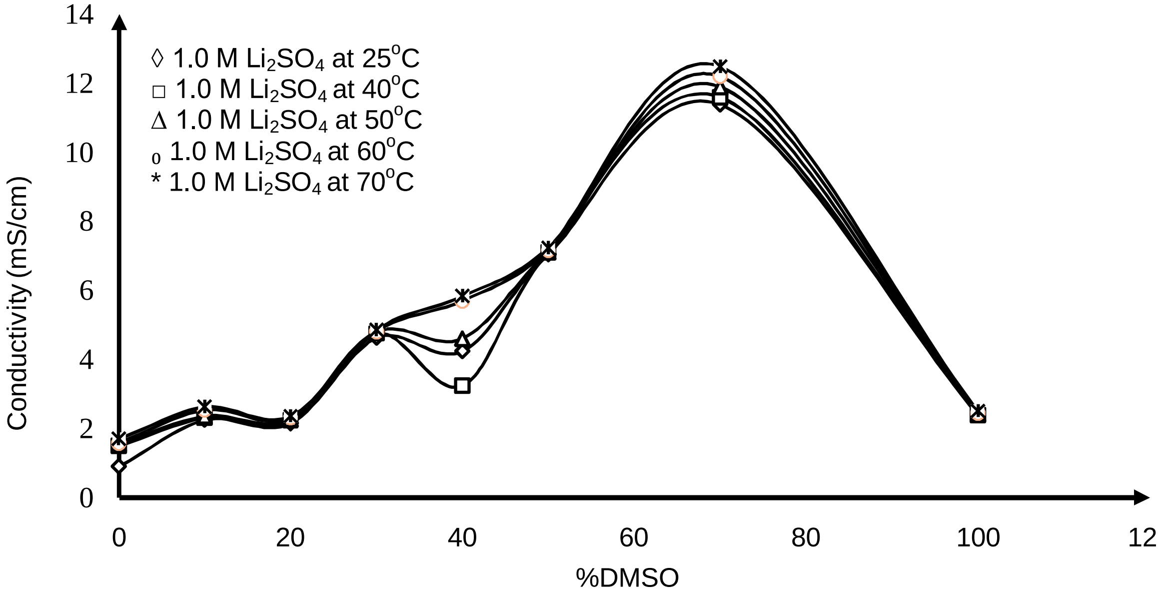

Fig. 7. Conductivity of 1.0M Li_2SO_4 with various %DMSO-THF mixtures at 25-70°C

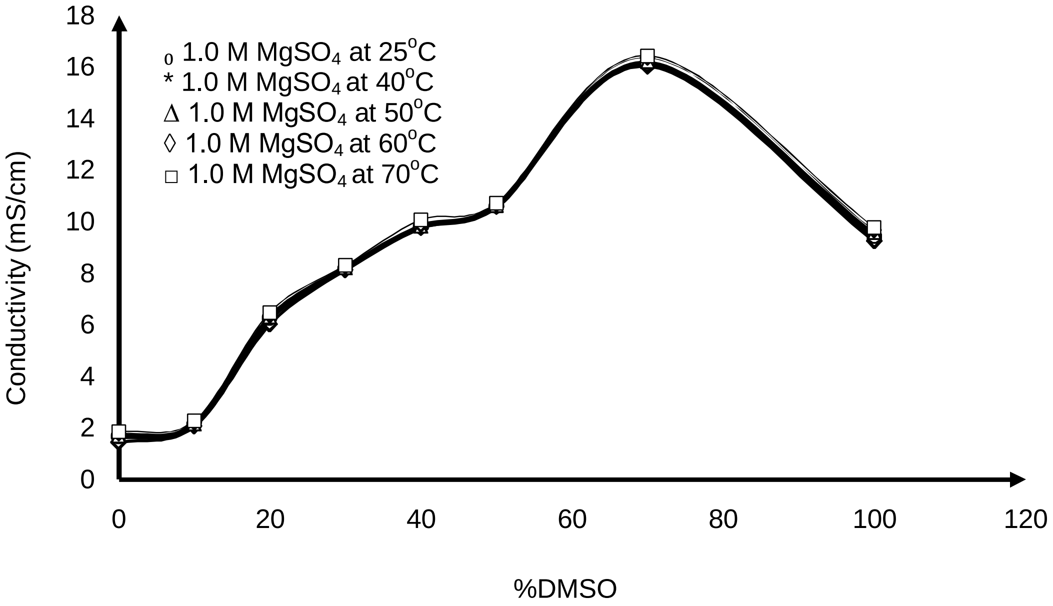

Fig. 8. Conductivity of 1.0M $MgSO_4$ with various %DMSO-THF mixtures at 25-70°C

Comparing the conductivity results obtained in DMSO-THF system containing 1.0 M of Li_2SO_4 and 1.0 M of $MgSO_4$, the system containing $MgSO_4$ gave the highest conductivity relative to the Li_2SO_4 system. This can be attributed to the differences in their electronic charge i.e., Mg^{2+} being greater than Li^+ as they moved through the solution (Ibezim-Ezeani *et al*. [22]

However, as the concentrations of Li_2SO_4 and $MgSO_4$ increased in the DMSO-THF system, the conductivity values increased [22]. The electrolyte solution containing $MgSO_4$ yields better conductivity than that containing Li_2SO_4 at high concentration of the salts.

3.2 Resistivity

The result revealed that minimum resistivity value was obtained at 40% DMSO without salt, 70% DMSO in 0.1 M Li_2SO_4, 70% DMSO in 0.5 M Li_2SO_4 and 70% DMSO in 1.0 M Li_2SO_4 in the DMSO-THF system respectively at 25°C (Figures 9-12). At increased temperature of 70°C, the minimum resistivity was obtained at 70% DMSO-THF in 0.1, 0.5 and 1.0 M Li_2SO_4 and $MgSO_4$ in the DMSO-THF system.

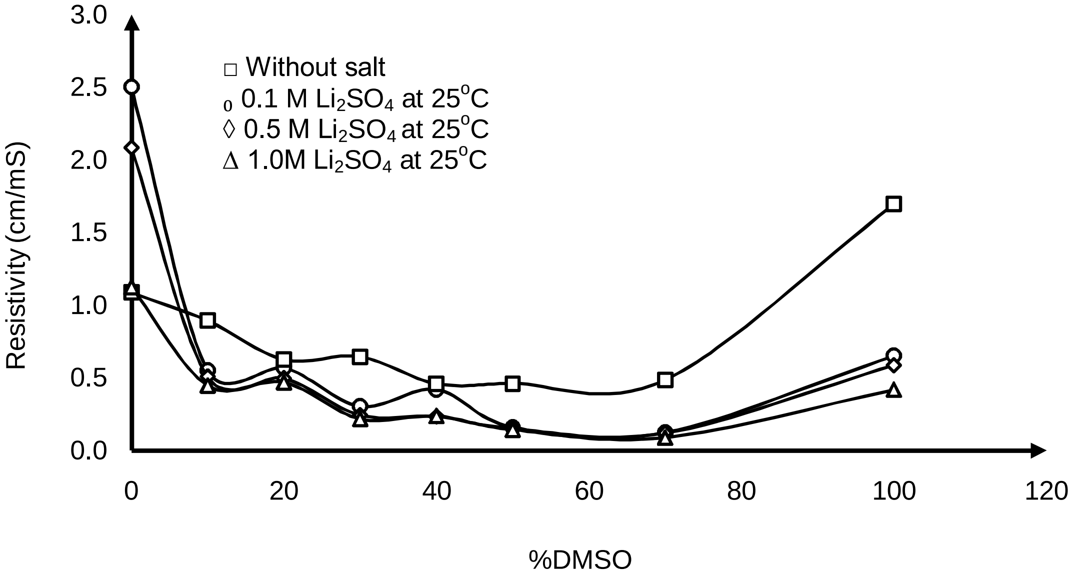

Fig. 9. Resistivity of Li_2SO_4 concentrations in %DMSO-THF mixtures at 25°C

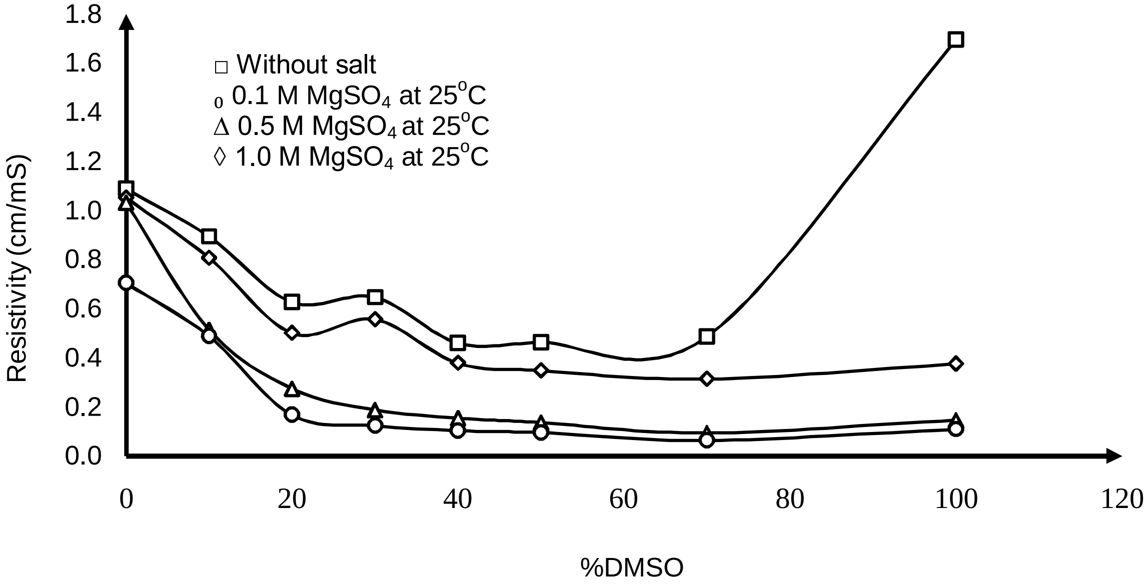

Fig. 10. Resistivity of $MgSO_4$ concentrations in %DMSO-THF mixtures at 25°C

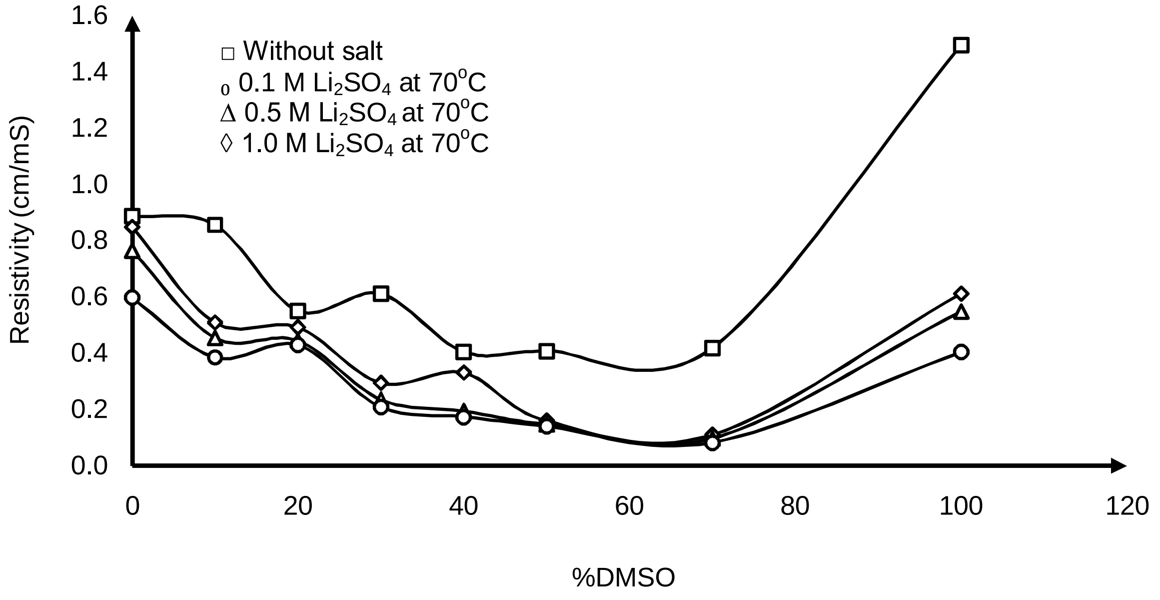

Fig. 11. Resistivity of Li_2SO_4 concentrations in various %DMSO-THF mixtures at 70°C

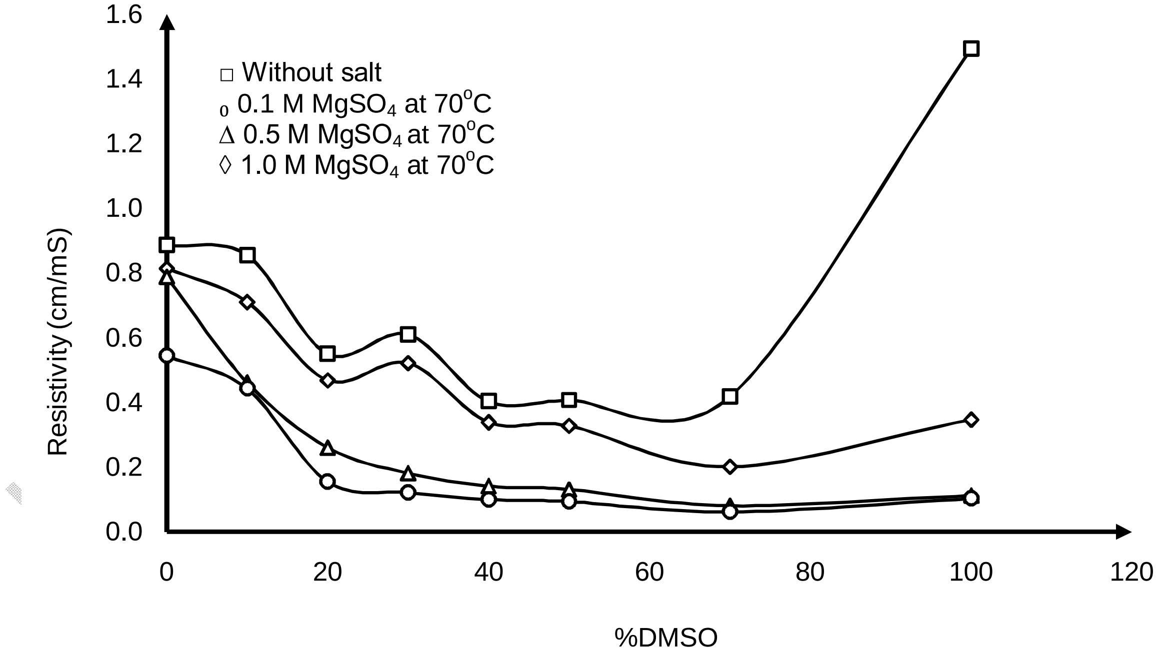

Fig. 12. Resistivity of $MgSO_4$ concentrations in various %DMSO-THF mixtures at 70°C

3.3 Electrochemical Cell Voltage

The measured electrochemical cell voltages of Li_2SO_4-DMSO-THF system at 25°C (Tables 2) showed maximum cell voltage at 50% DMSO in 0.1 M Li_2SO_4 while the measured electrochemical cell voltages of $MgSO_4$-DMSO-THF system at 25°C (Table 3) showed maximum cell voltage at 20% DMSO in 1.0 M $MgSO_4$. In 2000, Anusiem postulated that cell potential in concentration cells is dependent on the difference in concentration of ions in the cells [23].

Table 2. Cell Voltages and Free Energies for DMSO-THF system with various concentrations of Li_2SO_4 at 25°C

% DMSO	without salt		with 0.1 M salt		with 0.5 M salt		with 1.0 M salt	
	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

3.4 Gibbs Free Energy

The deduced values of $-\Delta G$ 3 for Li_2SO_4-DMSO-THF and $MgSO_4$-DMSO-THF systems respectively was obtained from the expression in equation 1.

$$-\Delta G = nFE^{o} \quad (1)$$

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

The results in Tables 2 and 3 revealed higher negative ΔG values for $MgSO_4$-DMSO-THF system than Li_2SO_4-DMSO-THF system, which suggest greater tendency for redox reaction within the electrode-electrolyte compartment to produce higher potential difference between the electrodes in the case of magnesium cell than lithium cell [22].

Table 3. Cell Voltages and Free Energies for DMSO-THF system with various concentrations of $MgSO_4$ at 25°C

% DMSO	without salt		with 0.1 M salt		with 0.5 M salt		with 1.0 M salt	
	E_{cell} (V)	− ΔG (kJ)	E_{cell} (V)	− ΔG (kJ)	E_{cell} (V)	− ΔG (kJ)	E_{cell} (V)	− ΔG (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 thermodynamic behavior of the mixed organic solvents 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 voltages in magnesium battery system than in lithium battery system, and at increased percentage of DMSO 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 Li_2SO_4 salt and 30%-70% DMSO for $MgSO_4$ salt. Conductivity increased with increase in the concentrations of salts in the binary systems. This study showed that the mixing of organic solvents of DMSO-THF improved the performance behavior of the pure organic solvents, thereby making them suitable for use as electrolytes in lithium and magnesium cells.

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