

Original Research Article

Effect of Mg^{2+} And Li^+ concentration on electrical conductivity of Dimethyl Sulfoxide-Tetrahydrofuran Binary mixture for fabricating Mg and Li based energy storage devices

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.

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 Li^+ ion concentration and 20%-70% DMSO for Mg^{2+} concentration. The result revealed greater tendency for redox reaction within the electrode-electrolyte region of Mg^{2+} -DMSO-THF.

Conclusion: This research has provided a new set of data on the parameters measured for battery fabrication with Mg^{2+} performing relatively better than 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 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 dimethylsulfoxide (DMSO, Sigma-Aldrich, 99.50%), tetrahydrofuran (THF, Sigma-Aldrich, 99.50%), magnesium sulphate (MgSO_4 , Sigma-Aldrich, 99.95%), and lithium sulphate (Li_2SO_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 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 electrolytes 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

voltage were measured at the same different concentrations using a digital multimeter as shown in Figure 1.

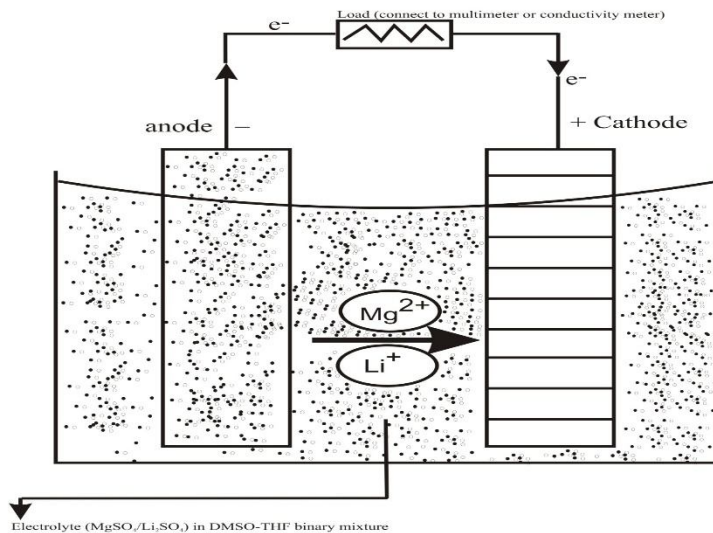


Fig. 1. Electrochemical set-up

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 electrolytes in the DMSO-THF binary system (Figures 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.

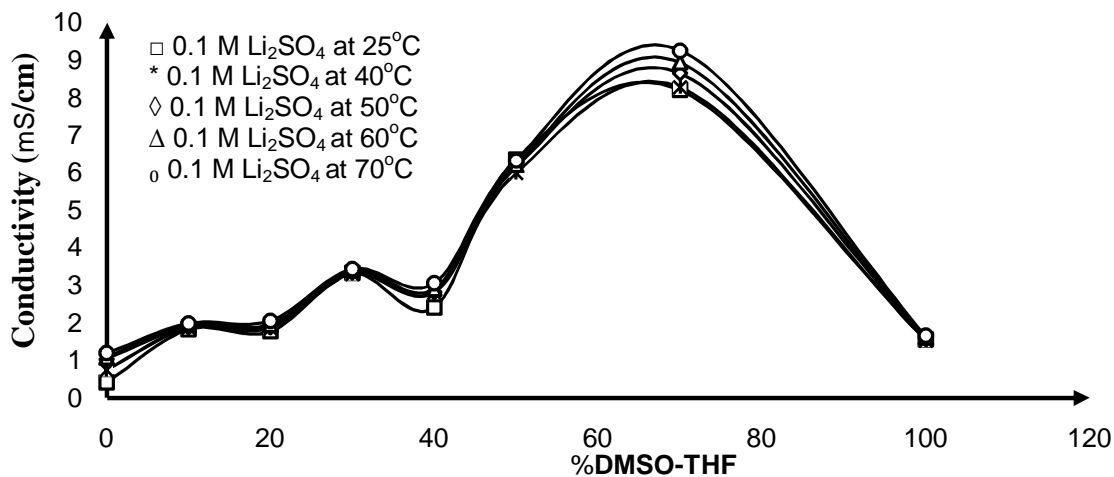


Fig. 2. Conductivity of 0.1M Li_2SO_4 with various %DMSO-THF mixtures at 25-70°C

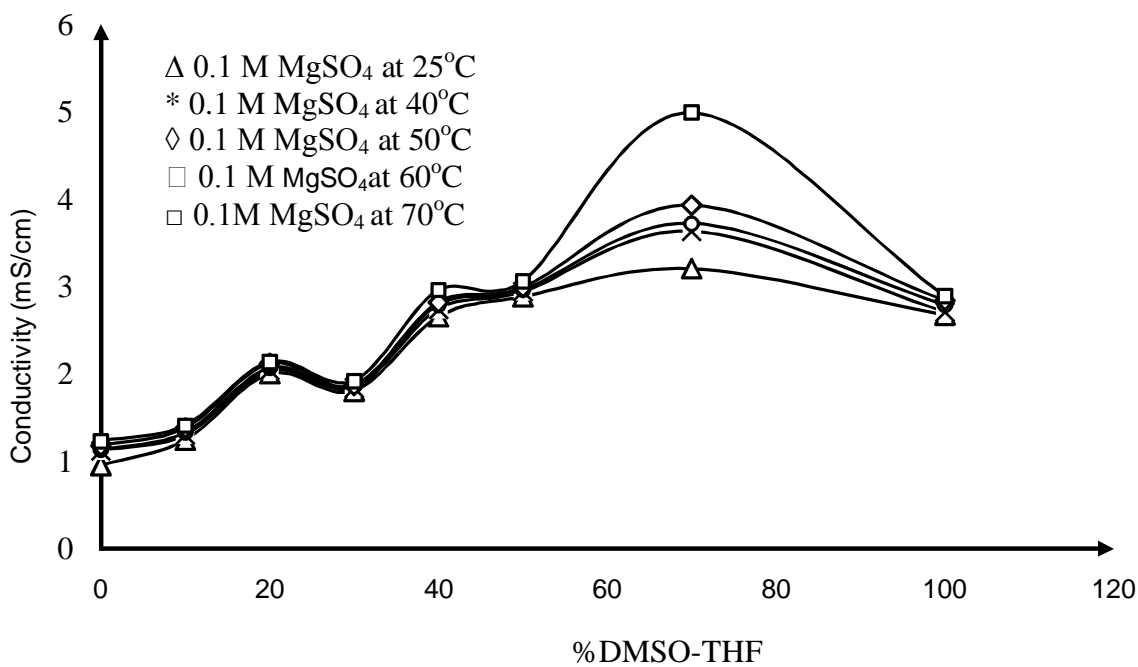


Fig. 3. Conductivity of 0.1M MgSO_4 with various %DMSO-THF mixtures at 25-70°C

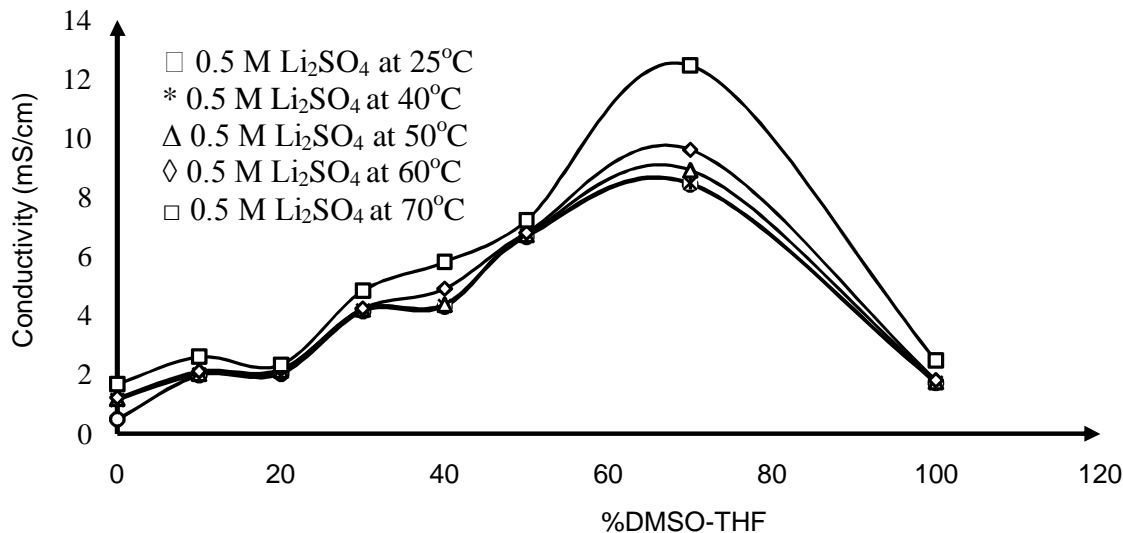


Fig. 4. Conductivity of 0.5M Li₂SO₄ with various %DMSO-THF mixtures at 25-70°C

The result of this study reveals that maximum conductivity was obtained at 70% DMSO in 1.0 M MgSO₄ 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.

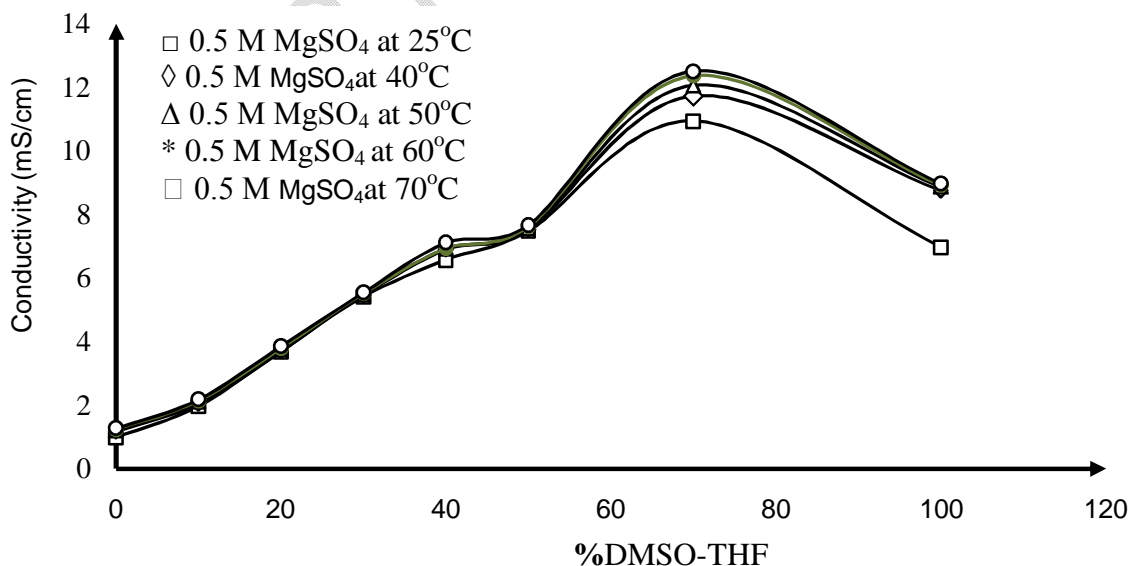


Fig. 5. Conductivity of 0.5M MgSO₄ with various %DMSO-THF mixtures at 25-70°C

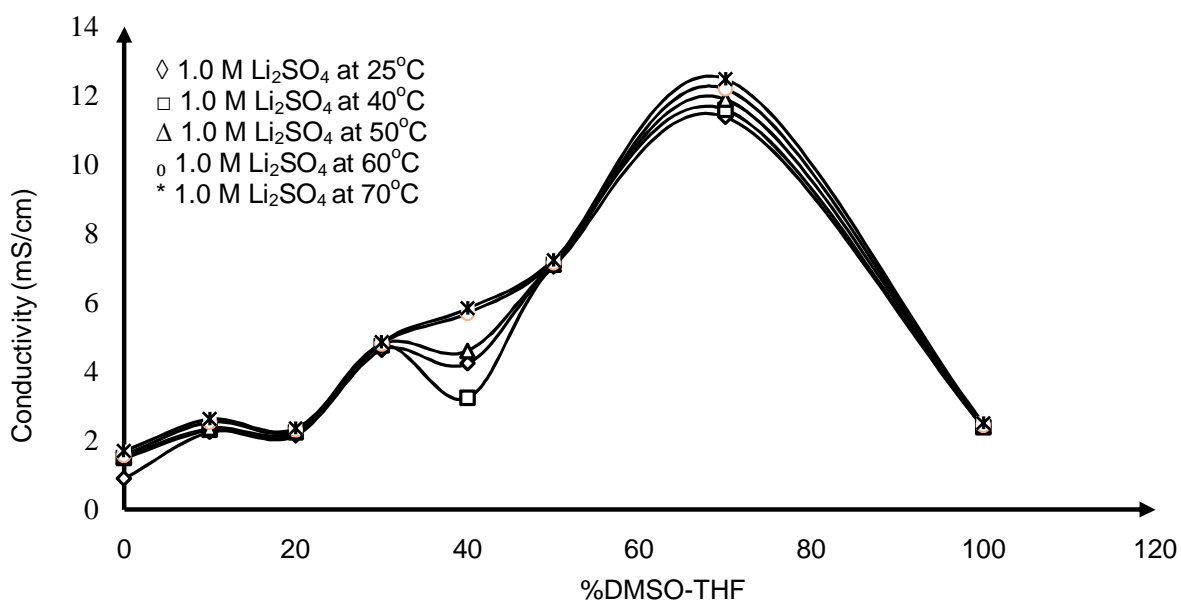


Fig. 6. Conductivity of 1.0M Li_2SO_4 with various %DMSO-THF mixtures at 25-70°C

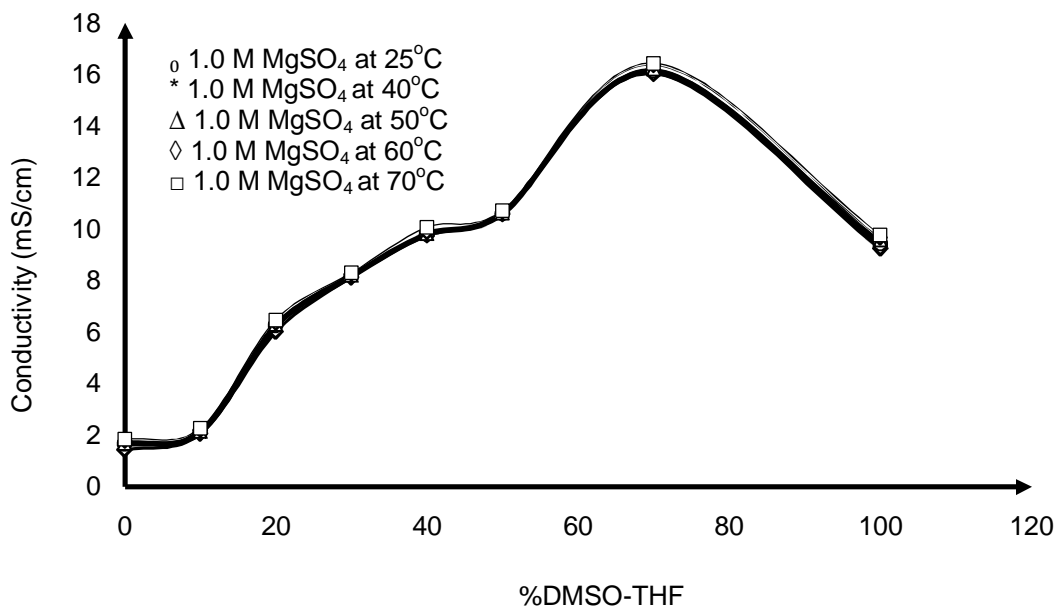


Fig. 7. Conductivity of 1.0M MgSO_4 with various %DMSO-THF mixtures at 25-70°C

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 concentrations.

3.2 Resistivity

The result revealed that minimum resistivity value was obtained at 70% DMSO with 1.0 M MgSO_4 (Figure 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^{2+} and Li^+ ions (Figures 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^{2+} ion showed higher conductivity than the Li^+ ion.

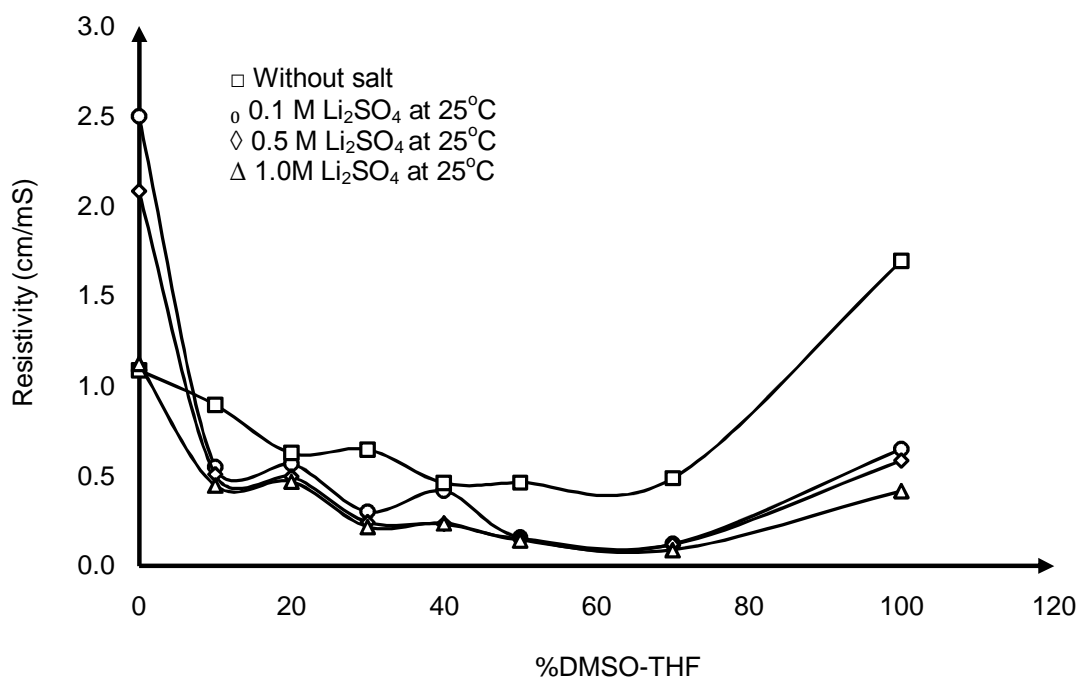


Fig. 8. Resistivity of Li_2SO_4 concentrations in %DMSO-THF mixtures at 25°C

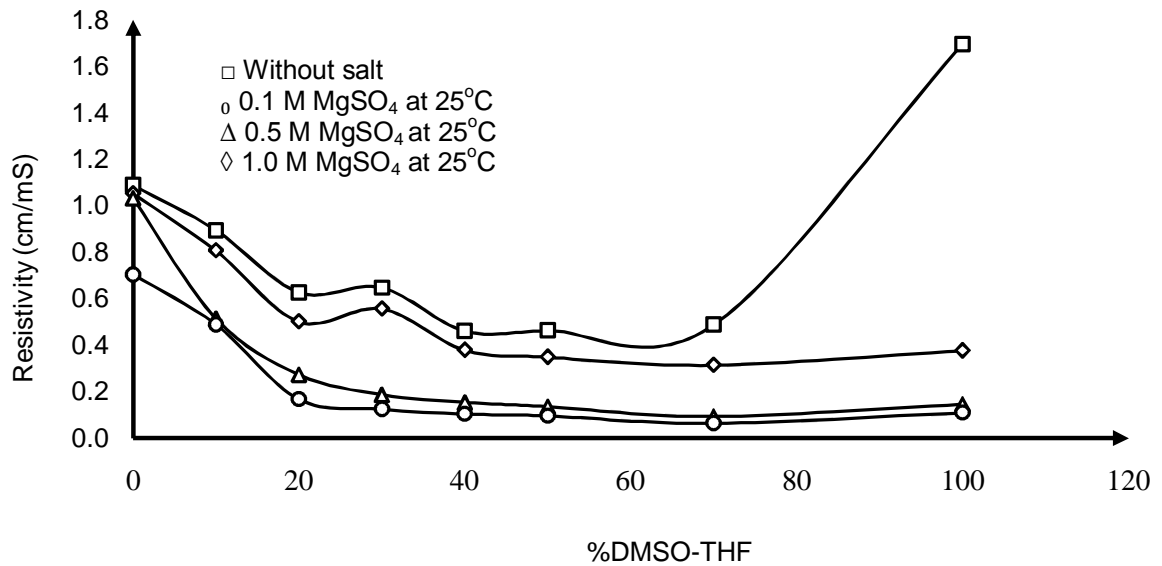


Fig. 9. Resistivity of MgSO_4 concentrations in %DMSO-THF mixtures at 25°C

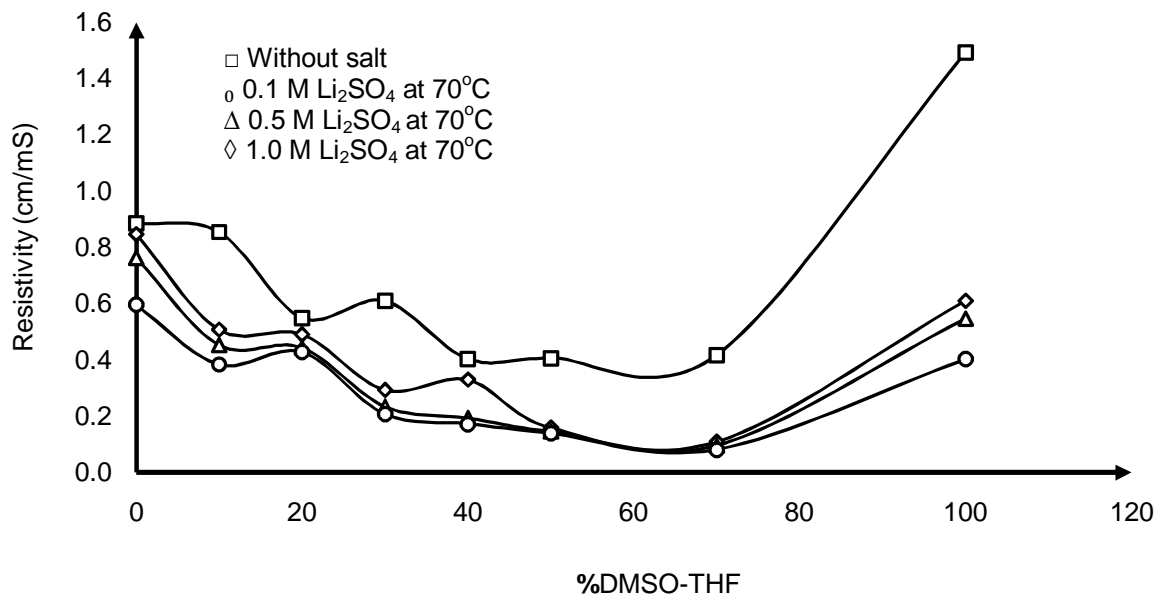


Fig. 10. Resistivity of Li_2SO_4 concentrations in various %DMSO-THF mixtures at 70°C

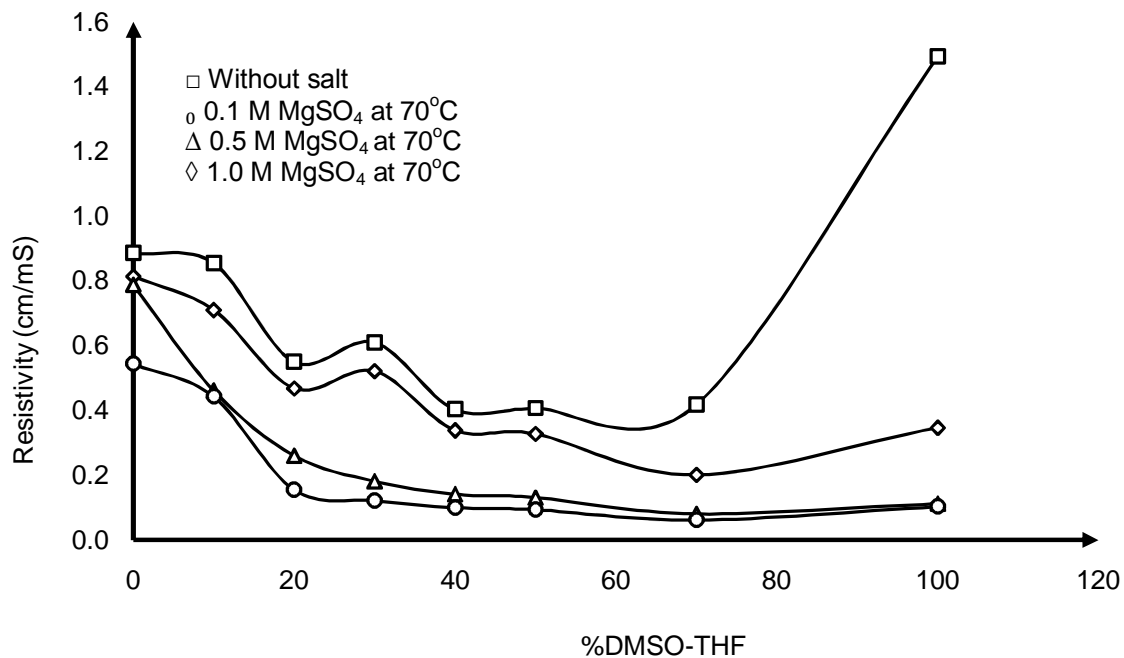


Fig. 11. Resistivity of MgSO₄ concentrations in various %DMSO-THF mixtures at 70°C

3.3 Electrochemical Cell Voltage

The measured electrochemical cell voltage of Li₂SO₄-DMSO-THF system at 25°C (Tables 2) showed maximum cell voltage at 50% DMSO-THF in 0.1 M Li₂SO₄ while the measured electrochemical cell voltage of MgSO₄-DMSO-THF system at 25°C (Table 3) showed maximum cell voltage at 20% DMSO-THF in 1.0 M MgSO₄. The measured electrochemical cell voltage of the system revealed optimum value at 20% DMSO-THF with 1.0 M Mg²⁺ ion. In 2000, Anusiem postulated that cell voltage in concentration cells is dependent on the difference in concentration of ions in the cells [23].

% DMSO	without ion	with 0.1 M	with 0.5 M	with 1.0 M
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	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 2. Cell voltage and free energy for DMSO-THF system with various concentrations of Li^+ at 25°C

3.4 Gibbs Free Energy

The deduced values of Gibbs free energy change ($-\Delta G$) for Li_2SO_4 -DMSO-THF and MgSO_4 -DMSO-THF systems respectively was obtained from the expression in equation 1.

$$-\Delta G = nFE^0 \quad (1)$$

Where, n = Number of moles of electrons transferred (1 and 2 for Li^+ and Mg^{2+} respectively)
 F = Faraday's constant ($\approx 96500 \text{ Cmol}^{-1}$), 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 (spontaneity) for redox reaction within the electrode-electrolyte compartment to produce higher potential difference [22]. This result is an improvement on the stability and safety performance using DMSO-THF binary mixture.

Table 3. Cell voltage and free energy for DMSO-THF system with various concentrations of Mg^{2+} at 25°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 Li^+ ion and 20%-70% DMSO for 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.

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