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# Characteristic Behavior of Lithium and Magnesium Perchlorate Salts in Binary Organic System Followed Conductometrically

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**Abstract:** ***The conductivity of lithium and magnesium ions in mixed electrolyte systems of 1,2-dimethoxyethane (DME) and ethylene carbonate (EC) was investigated. The organic electrolyte solutions were prepared by mixing varied volume ratios of DME and EC with varying concentrations of lithium and magnesium perchlorate salts. The conductivities, cell voltages and Gibbs free energy of the redox reaction were determined. Comparing the molar conductivities of these two salts measured at 25 °C in the mixed DME-EC system, 0.5M $Mg(ClO_4)_2$ gave more molar conductivity of 28.68 $mScm^{-1}$ against 26.85 $mScm^{-1}$ of $LiClO_4$. However, at relatively higher concentrations (1.0M and 2.0M), $LiClO_4$ yielded better molar conductivity results than $Mg(ClO_4)_2$. Cell voltage was highest in the $Mg(ClO_4)_2$-DME-EC system with a value of 0.87 volts and 0.74 volts for $LiClO_4$-DME-EC system. The negativity of Gibbs free energy was also highest for $Mg(ClO_4)_2$-DME-EC (-167.910 kJ/mol at 40 % DME), while that of $LiClO_4$-DME-EC was -71.410 kJ/mol at 60 % DME. This indicates greater spontaneity of $Mg(ClO_4)_2$-DME-EC cell reaction. The mixing ratio of the DME-EC system for optimum battery performance was resolved to be 60 % DME for $LiClO_4$ salt and 40 % DME for $Mg(ClO_4)_2$ salt. The interpretations of experimentally deduced results were based on the influence of ion-solvent and solvent-solvent interactions in the DME-EC system.***

**Keywords:** Conductivity, dimethoxyethane-ethylene carbonate system, battery, cell voltage, concentration cell, Gibbs free energy, perchlorate salt

## 1. Introduction

The capacity of current transmission in a given aqueous or non-aqueous solution with time reflects the flow of certain quantity of charged species, and in turn its conductivity. The principles governing the conductivity of ions within a system have recorded tremendous successes in electrochemical processes and electro-analytical measurements [1], [2], [3]. In applications involving conductivity or conductometric methods therefore, continuous monitoring of system temperature, redox behavior of ions, rheological nature of charged particles and the amount of ions per volume of reaction mixture is crucial in order to forestall any negative impact on its operational efficiency. A study on the characteristic behavior of lithium and magnesium perchlorate salts in binary organic system was undertaken. The development of advanced secondary lithium batteries is faced with the challenge of solvation of its ions in electrolyte solution [4] [5]. Earlier studies remarked that an ion-permeable film was formed at the phase boundary between negative electrodes and electrolyte solutions of secondary lithium batteries [6]. Normally, two electrons are transferred by Mg ion per its atom in an electrochemical cell, as compared to one electron transferred by Li ion. This would infer that the metal anode composed of Mg will supply energy density higher than that of Li [7]; and as a result produce longer lasting power output device. A review of existing literature revealed that the volumetric energy density of an anode consisting of solid Mg is ~3833 mAhcm-3, compared to ~800 mAhcm-3 for Li insertion into graphite [8]. The conductivity of dissolved LiClO4 in mixed organic electrolyte system of propylene carbonate and 1,2-dimethoxyethane was investigated at 30°C. Changes in relative permittivity and viscosity of the mixture influenced the conductivity of the electrolyte solution. The experimental findings were accounted for based on the ion-solvent and solvent-solvent interactions which contributed to the enhancement of the ionic conductance [9]. Revelations from chronoamperometry study noted that all liquid electrolytes have only ionic movements for conductivity and negligible amount of electrons[10]. Thus, in designing batteries with long lasting efficacy, the incorporation of solvents of low viscosity and high dielectric constant into the electrolyte system is of the essence [11].

The target of this work is to comparatively study the conductivities, cell voltages and Gibbs free energies of $LiClO_4$-DME-EC and $Mg(ClO_4)_2$-DME-EC systems; and to apply the findings as basis for the development of advanced lithium and magnesium batteries of very high standard.

## 2. Experimental

The solvents, ethylene carbonate (EC) (98 %) and 1,2-dimethoxyethane (DME) ( > 99 %) and the salts, lithium perchlorate ($LiClO_4$) ( > 95.0 %) and magnesium perchlorate [$Mg(ClO_4)_2$] (95 %) were commercially obtained from Sigma Aldrich. The solvents were utilized without further purification since the experimentally determined values of density are in line with literature report. Varying volume proportions of binary mixtures of the solvents (DME-EC) were prepared as follows: 100, 80, 70, 60, 50, 40, 30 and 20 % of DME [12]. Solutions of 0.5M, 1.0M, and 2.0M concentration of $Mg(ClO_4)_2$ and $LiClO_4$ salts were prepared in various DME-EC solvent proportions.

## 3. Results and Discussion

### 3.1 Conductivity Study

Basically, the conductivity of electrolyte solution reflects the level of its ionic concentration, measure of dielectric constant and viscosity behavior of the system. The conductivity results for both $Mg(ClO_4)_2$ and $LiClO_4$ salts in the DME-EC binary system show increase in the conductivity values of the varying molar concentrations of both $Mg(ClO_4)_2$ and $LiClO_4$ salts in the DME-EC system as the percentage composition of EC in the mixtures increase. However, the observed increment is not monotonous. Maximum conductivity values were observed in all the DME-EC systems containing various concentrations of $Mg(ClO_4)_2$ and $LiClO_4$ salts.

These deviations from the monotonous increase may be attributed to both the increase in the dielectric constant and increase in the viscosity of the medium as a result of the sequential increase in the volume of EC component and decrease in the volume of DME in the DME-EC system.

Increasing the EC content of the mixtures would obviously increase the dielectric constants of the system which will in turn favor the effective dissociation of ions. On the other hand, a decrease in the DME component would increase the viscosity of the system thereby reducing the mobility of ions present in the medium. This accounts for the observed decline in the conductivities of the system with decrease in DME component.

For the DME-EC system containing $LiClO_4$ salt, maximum conductivity was obtained at 60 % DME in 0.5M $LiClO_4$, 70 % DME in 1.0M $LiClO_4$ and 70 % DME in 2.0M $LiClO_4$, while for the $Mg(ClO_4)_2$ salt system, maximum conductivity was obtained at 40 % DME in 0.5M $Mg(ClO_4)_2$, 50 % DME in 1.0M $Mg(ClO_4)_2$ and 40 % DME in 2.0M $Mg(ClO_4)_2$.

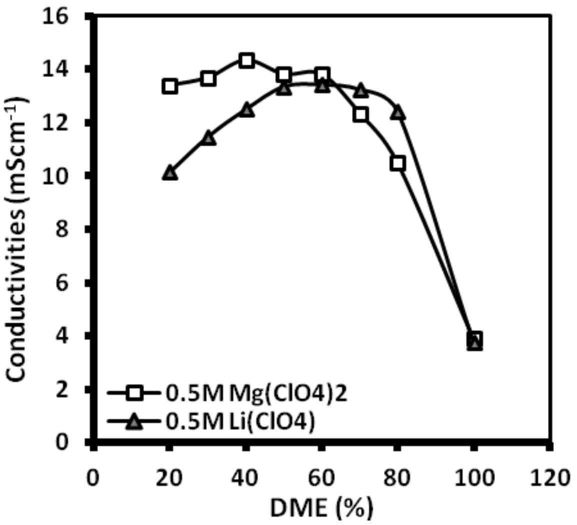

**Figure 1:** Conductivities of 0.5M $Mg(ClO_4)_2$ and 0.5M $LiClO_4$ in the DME-EC system at 25°C

Comparing the conductivity results obtained in DME-EC system containing 0.5M of $LiClO_4$ (a uni – univalent electrolyte) and 0.5M $Mg(ClO_4)_2$ (a uni – bivalent electrolyte), the system containing $Mg(ClO_4)_2$ gave the highest conductivity relative to the $LiClO_4$ system. This can be attributed to the fact that $LiClO_4$ is a uni – univalent electrolyte (1:1) while $Mg(ClO_4)_2$ is a uni – bivalent electrolyte (2:1). $Mg^{2+}$ ion which is doubly charged carries twice as much current as $Li^+$ ion which is singly charged as they move through the solution.

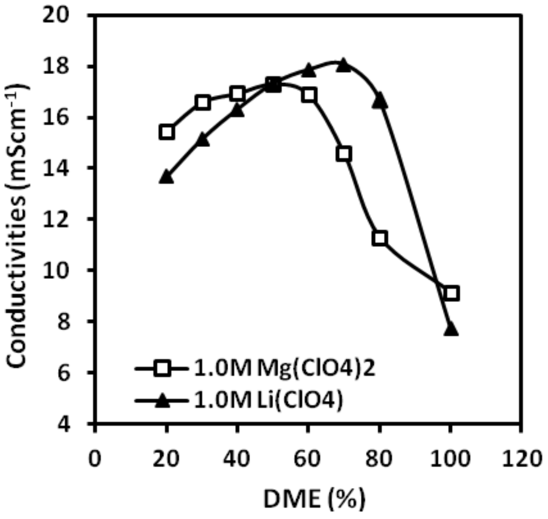

**Figure 2:** Conductivities of 1.0M $Mg(ClO_4)_2$ and 1.0M $LiClO_4$ in the DME-EC system at 25° C

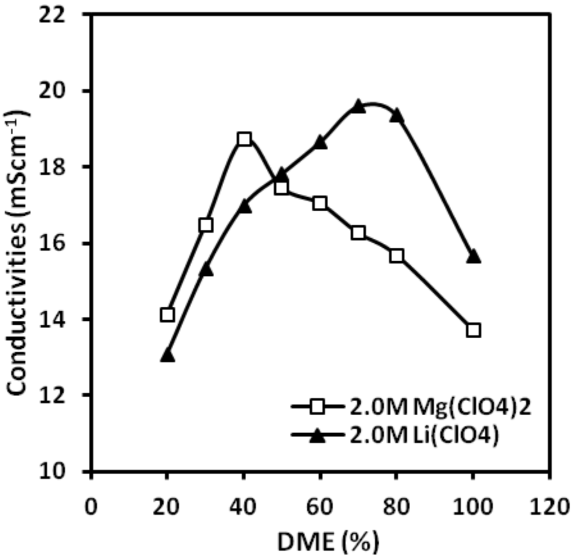

**Figure 3:** Conductivities of 2.0M $Mg(ClO_4)_2$ and 2.0M $LiClO_4$ in the DME-EC system at 25° C

However, as the concentration of $Mg(ClO_4)_2$ and $LiClO_4$ increased in the DME-EC system, the electrolyte solution containing $LiClO_4$ yielded better conductivity result than that of $Mg(ClO_4)_2$. This is illustrated in figure 3 and can be attributed to the fact that $Mg(ClO_4)_2$ salt which has a relatively high molecular weight than $LiClO_4$ will dissociate effectively in a solvent mixture of relatively high dielectric constant. The results also suggest a possible formation of ion-association or ion – pairs in the $Mg(ClO_4)_2$ systems at a higher concentration. A possible deduction here is that $Mg(ClO_4)_2$ salt yields better conductivity result at a lower concentration while $LiClO_4$ salt conducts better at relatively high concentrations.

Earlier study hinted that increase in viscosity, electrophoretic and relaxation effects contribute to decrease in conductivity [9].

### 3.2 Electrochemical cell voltage

Concentration cells were constructed with Mg electrode for the magnesium salt solutions and graphite electrode for the lithium salt solutions. The cell voltage ($E_{cell}$) was measured with the voltmeter attached to the concentration cell. The electrochemical cell notation for the $Mg(ClO_4)_2$- and $LiClO_4$-DME-EC systems can be written as follows:

Magnesium / 0.1 M $Mg(ClO_4)_2$-DME-EC // 1.0 M $Mg(ClO_4)_2$-DME-EC / Magnesium
Graphite / 0.1 M $LiClO_4$-DME-EC // 1.0 M $LiClO_4$-DME-EC / Graphite

In the concentration cells for $Mg^{2+}$ and $Li^{+}$ solutions, 1.0 M and 0.1 M concentrations were used for the cathode and anode compartments respectively. The cells exhibited positive voltages as a consequence of the difference in concentrations in both compartments (Tables 1 and 2).

**Table 1:** Cell Voltages and Free Energies For The $Mg(ClO_4)_2$-DME-EC System

| DME (%) | $E_{Cell}$ (Volts) | -ΔG (kJ) |
|---|---|---|
| 100 | 0.28 | 24.125 |
| 80 | 0.34 | 30.880 |
| 70 | 0.48 | 49.215 |
| 60 | 0.62 | 71.410 |
| 50 | 0.73 | 46.320 |
| 40 | 0.87 | 40.530 |
| 30 | 0.65 | 32.810 |
| 20 | 0.42 | 27.020 |

**Table 2:** Cell Voltages and Free Energies For The $LiClO_4$-DME-EC System

| DME (%) | $E_{Cell}$ (Volts) | -ΔG (kJ) |
|---|---|---|
| 100 | 0.25 | 54.040 |
| 80 | 0.32 | 65.620 |
| 70 | 0.51 | 92.640 |
| 60 | 0.74 | 119.660 |
| 50 | 0.48 | 140.890 |
| 40 | 0.42 | 167.910 |
| 30 | 0.34 | 125.450 |
| 20 | 0.28 | 81.060 |

The highest cell voltage was found to be 0.87 volts for the $Mg(ClO_4)_2$-DME-EC system, while 0.74 volts was for $LiClO_4$-DME-EC system

The feasibility of the redox reaction involving the transfer of electrons in the concentration cells was determined using Gibbs free energy (-ΔG) equation (1) [13]:

$$-\Delta G = nFE_{cell} \tag{1}$$

Where n is number of moles of electrons transferred, and F is faraday constant (≈96500 C/mol). The deduced values of -ΔG are presented in Tables 1 and 2 for $Mg(ClO_4)_2$- and $LiClO_4$-DME-EC systems respectively. The negative values of Gibbs free energy change were plotted as a function of volume ratios of DME-EC mixtures and depicted in Fig. 4.

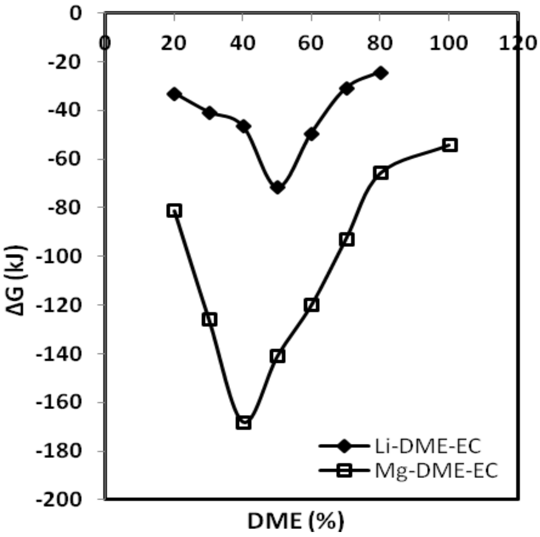

**Figure 4:** Gibbs free energy change as a function of DME at 25° C

The plots reveal higher negative ΔG values for $Mg(ClO_4)_2$- than $LiClO_4$-DME-EC system, which suggest greater tendency for redox reaction within the electrode-electrolyte compartment to produce potential difference between the electrodes in the case of magnesium than lithium.

## 4. Conclusion

Different volume ratios of DME-EC mixtures were prepared and investigated with varying concentrations of both $LiClO_4$ and $Mg(ClO_4)_2$ salts. The results show that Molar conductivities of both $LiClO_4$ and $Mg(ClO_4)_2$ in DME-EC system rose with increase in EC component of the mixtures, suggesting a possible rise in relative permittivity of the medium as the percentage composition by volume of EC increases. The solution containing 0.5M $LiClO_4$ salt gave superior molar conductivity results over other analogous systems containing 1.0M and 2.0M salt concentrations. This shows that increase in concentration introduces more ions into the electrolyte system thereby inducing stronger molecular and ionic interactions emerging as a result of electrophoretic effect. The highest cell voltage was found to be 0.87 volts for the $Mg(ClO_4)_2$-DME-EC system, while 0.74 volts was for $LiClO_4$-DME-EC system. The feasibility of the oxidation-reduction reaction to occur was higher for the magnesium than lithium system. The mixing ratio of the DME-EC system for optimum battery performance was established between 40 % DME for $Mg(ClO_4)_2$ salt and 60 % DME for $LiClO_4$ salt. The results obtained have been interpreted on the basis of intermolecular interactions such as ion-solvent and solvent-solvent interactions between component molecules of the system.

## 5. Acknowledgment

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