CELL POTENTIAL AND FREE ENERGY OF ELECTROLYTE SOLUTIONS OF MAGNESIUM BOROHYDRIDE SALT IN MIXTURES OF 2-METHOXYETHYL ETHER-PROPYLENE CARBONATE AND 1,2-DIMETHOXYETHANE-PROPYLENE CARBONATE

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ABSTRACT

This study explores the outcome of mixed solvent systems of 2-Methoxyethyl ether (DGM)-Propylene carbonate (PC) and 1,2-dimethoxyethane (DME)-Propylene carbonate (PC) on the electrochemical performance of concentration cells in order to construe the behaviour of ions in the electrolyte medium. Organic electrolyte solutions of Magnesium borohydride salt were constituted with concentrations of 0.01 and 0.001 M in the binary mixtures of DGM-PC and DME-PC. The values of the cell potential measured at 298.15 K were found to increase over the composition range of 0 –50 % volume for DME and DGM; and then decrease over the range of 50 – 100 % volume for DME and DGM. The cell potential for the DME-PC system reached the maximum value at 0.448 mole fraction DME, while that for the DGM-PC system was 0.374 mole fraction DGM. The Gibbs free energy change ranged from -6.832 to -8.396 kJ/mol and -6.967 to -8.685 kJ/mol for DME-PC and DGM-PC systems respectively. The calculated values of Gibbs free energy change were more negative for DGM-PC than the DME-PC system signifying the spontaneity of the cell reactions, which is more pronounced in the case of DGM-PC system. The standard cell potential measured from 0.006 to 0.014 V for DME-PC, and 0.007 to 0.0015 V for DGM-PC within the tested range. The standard cell potential were higher in DGM-PC than DME-PC, suggesting better coordination with the three lone electron pairs on the oxygen atoms of DGM molecules, which afforded higher complex stability with Mg^{2+} and reaction rates for DGM-PC system.

Keywords: Cell potential, Gibbs free energy change, Concentration cell, Organic electrolyte, Solvated structure.

INTRODUCTION

The interfacial chemistry between electrolyte and electrodes directs the performance of electrochemical systems. The chemical attributes of the electrodes usually determine the energy output, while the electrolyte defines the rate of energy release by regulating the rate of mass flow into the battery. Technically therefore, the electrolyte should demonstrate sufficient stability against electrochemical oxidation and reduction. Many battery systems succumb to the problem of low capacity as the battery undergoes repeated charge and discharge. The cell potential is related to the difference between the working operations

of anode and cathode (Manthiram, 1997), and the development of Chevrel-phase cathode active materials for magnesium batteries now ensures reversibility of the battery (Levi, et al. (2009). With this achievement, magnesium batteries have received increased attention as substitutes capable of overcoming the challenges of safety, cost and poor performance associated with lithium batteries. However, the energy density of magnesium batteries at the time of development fell short of that for lithium systems (Tao *et. al*., 2004; Le et. al., 1998). The need therefore for novel cathode material and compatible electrolytes remain critical for advancement of battery technology. The thermodynamic properties of magnesium put this metal in the fore-front for consideration as anode material. The attributes of magnesium range from the absence of dendrites during charging cycles, while the down-side reveals a more positive reduction potential in comparison to lithium metal. The absence of practical anode materials constitutes a major drawback in the development of high energy density rechargeable magnesium batteries. The development of magnesium batteries offers prospect for research collaboration between scientists and engineers. Such collaboration will facilitate the process of identifying and overcoming setbacks in developing magnesium battery systems. Furthermore, the prominence of this field of study focuses on developing new electrolytes as their properties regulate the choice of cathode materials (Muldoon *et. al*., 2012). The prospect of utilizing magnesium as anode material in high energy density batteries continues to spur interest in non-aqueous electrochemistry of

magnesium. The feasibility of rechargeable non-aqueous magnesium batteries has been reported. The solubility of magnesium salts in conventional electrolytes such as $Mg(ClO_4)_2$ constituted with non-aqueous solvents (ethers, alkyl carbonates and esters), is lower than that of Li salts (Gregory *et. al*., 1990). Electric current is simultaneously carried by both positive and negative ions in electrolyte, and the quantity of electricity carried is determined by the concentration and velocity of the ions (Atkins, 1998). Organic electrolytes containing mixed solvents have often been employed as electrolyte solutions in magnesium battery systems. The mixing processes can lead to new consequences that impact volume behaviour such as structural changes of components of mixture and intermolecular attraction or repulsion between unlike molecules. Magnesium borohydride electrolytes prepared with polyethers such as DGM have been employed in Mg batteries (Mohtadi *et al*., 2012). The present work aims at studying the correlation between solution composition and the electrochemical behaviour of Mg ions in two mixed solvents of DME-PC and DGM-PC systems. The ability of the solvents to bestow electron pair to a cation are invaluable in chemical bonding, while the high dielectric constant of PC helps to dissociate the salt; and the low viscosity of DME and DGM promotes the motion of ions in solution.

MATERIALS AND METHODS

DGM (99.5%) [BASF Chemical Company England], Dry $Mg(BH_4)_2$ (95%) [Sigma Aldrich], DME (99.5%) and PC (99.5%) [BDH Chemical Ltd. England] were used

without further purification. The kinematic viscosity of the solutions was measured at 298.15 K using a suspended ubbelohde viscometer tube ASTM D 446. The flow time was determined electronically by using an electronic timer with precision ± 0.01 s. The kinematic viscosity was calculated using the formula in equation 1 (Ibezim-Ezeani *et al.*,2017a):

$$V = kt \qquad (1)$$

Where V is the kinematic viscosity, k is the viscometer constant and t the flow time. The kinematic viscosity was converted into dynamic viscosities by using equation 2:

$$\eta = V\rho \qquad (2)$$

Where η is the dynamic viscosity and ρ is density of the liquid. The process was repeated until three successive determinations were obtained within ±0.1 seconds. The potential of the concentration cells with salt bridge was measured at 298.15 K and atmospheric pressure with an EXCEL XL 830 L digital volt meter with precision ± 0.01 V. The cell potential was recorded after the reading of the digital voltmeter stabilized and the process was repeated until three successive readings were obtained within ± 0.01 V and the results averaged. The concentration cells are written as equations 3 and 4:

$$Mg \, / \, Mg(BH_4)_2 \, (0.01mol \, dm^{-3}), \, DME\text{-}PC \, // \, DME\text{-}PC, \, Mg(BH_4)_2 \, (0.001mol \, dm^{-3}) \, / \, Mg \qquad (3)$$

$$Mg \, / \, Mg(BH_4)_2 \, (0.01mol \, dm^{-3}), \, DGM\text{-}PC \, // \, DGM\text{-}PC, \, Mg(BH_4)_2 \, (0.001mol \, dm^{-3}) \, / \, Mg \qquad (4)$$

The Gibbs free energy change was calculated using equation 5 (Ibezim-Ezeani *et al.*,2017b):

$$\Delta G = -n_F E \qquad (5)$$

Where ΔG is the Gibbs free energy change, n is number of electrons transferred during oxidation / reduction process, F is the Faraday's constant and E is the cell potential.
The standard potential of the reaction in the cell $E°$ (volts) is given by equation 6:

$$E° = -\frac{\Delta G°}{nF} = \left(\frac{RT}{nF}\right) \ln K \qquad (6)$$

When the activities of the products and reactants are unity, ΔG° is the standard Gibbs free energy change, K is the equilibrium constant, R is the gas constant and T is the thermodynamic temperature.

The Nernst equation (Brown *et al.*, 2009) is given by equation 7, where Q is the reaction quotient:

$$E = E^0 - \frac{0.0257V}{n} \ln Q \qquad (7)$$

RESULTS AND DISCUSSION

Cell potential

The cell potential (E) values for DME-PC and DGM-PC mixed systems increased over the composition range of 0 – 50 % vol. for DME or DGM and decreased over the range of 50 – 100 % vol. for DME or DGM (Table 1 and 2). Equations 3 and 4 depict different concentration cells with the half-cells of lower concentration situated on the right-hand side. As electrons are transferred from the right half-cell (reduction) of low concentration to the left half-cell (oxidation) of high concentration, a voltage is generated. The right half-cell reaction proceeds as follows:

$$Mg \rightarrow Mg^{2+} + 2e^- \quad (6)$$
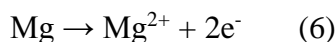
As Mg^{2+} ions begin to form in the right half-cell of low concentration, the concentration of the right half-cell increases and the cell reaction becomes more spontaneous and cell potential increases. Conversely, in the left half-cell, the reaction proceeds as written:

$$Mg^{2+} + 2e^- \rightarrow Mg \quad (7)$$
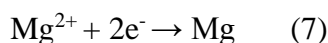
As Mg^{2+} ions begin to deplete in the left half-cell of high concentration, the concentration of the left-half-cell decreases and the cell reaction becomes less spontaneous and cell potential decreases. Furthermore, the observed increase in cell potential values over the constitution range of 0 – 50 % vol. for DME or DGM, may also be credited to the lower viscosity of the mixtures which facilitated ionic mobility (Ibezim-Ezeani *et al.*,2017a). This behavior may be aided by strong solvation of the ions in the solvent ligands. However, above the constitution range of 50 % vol., the cell potential dropped progressively, which may be attributed to decreasing dielectric constant of the mixture. This suggests that the growing strength of electrostatic attraction relative to ion-dipole interactions impede ion solvation and cell potential values declined over the constitution range of 50 – 100 % vol. of DME or DGM.

Table 1: Cell Potential and Gibbs free energy for DME-PC system at 298.15 K

% DME	Mole fraction	E (V)	ΔG (kJ/mol)
0	0.000	0.0398	-7.681
15	0.125	0.0414	-7.990
25	0.214	0.0420	-8.106
50	0.448	0.0435	-8.396
75	0.710	0.0430	-8.299
85	0.822	0.0416	-8.029
100	1.000	0.0354	-6.832

Table 2: Cell Potential and Gibbs free energy for DGM-PC system at 298.15 K

% DGM	Mole fraction	E (V)	ΔG (kJ/mol)
0	0.000	0.0406	-7.836
15	0.095	0.0423	-8.164
25	0.167	0.0434	-8.376
50	0.374	0.0450	-8.685
75	0.643	0.0444	-8.569
85	0.772	0.0426	-8.221
100	1.000	0.0361	-6.967

Gibbs free energy change

Observations from Tables 1 and 2 reveal that the values of ΔG are negative over the entire composition range confirming that the electrochemical reaction in the half-cells were spontaneous. The predominance of negative ΔG values could be attributed to dispersion forces between unlike molecules of DME-PC and DGM-PC (Ibezim-Ezeani and Menegbo, 2017; Obowu *et al.*, 2018a). The greater negativity of ΔG in the DGM-PC system implies that the DGM molecules are more polarizable than DME molecules. Consequently, the valence electrons in DGM molecules are easily displaced by the electric field of the Mg^{2+}; thus, the free energy requirement for the solvation of the Mg^{2+} is relatively lower for DGM-PC in comparison with that for DME-PC medium. As a result of the greater polarizability of DGM molecules, the electrolytes constituted with DGM-PC mixtures will exhibit better conductivity

(Ibezim-Ezeani *et al*., 2017b; Obowu *et al*., 2018b). The improved cell potential observed in Table 2 provides premise for this assertion and with better conductivity in the DGM-PC mixture, reversibility is optimized in the functionality of Mg battery systems. Consequently, when the DGM molecules are subjected to the ionic field of Mg^{2+}, their dipoles tend to orient with the least amount of free energy. Furthermore, DGM molecules have carbon-6 chain in comparison with the carbon-4 of DME molecules. The carbon-6 chain is the least sterically hindered and this factor contributes towards better coordination with Mg^{2+} when the metal ion bonds with the three donor atoms on DGM; thus, the strength and stability of the resulting magnesium complex is optimised.

Standard cell potential

The standard cell potential (E°_{cell}) was determined using the Nernst equation and the results are presented in Tables 3 and 4. The values of standard cell potential for both DME-PC and DGM-PC systems are positive over the entire tested range. This condition will invariably favour the formation of products, as the condition for positive value of equilibrium constant (K) is fulfilled (equation 6).

Table 3: Standard Cell Potential for DME-PC System

% DME	Mole fraction	E°_{cell} (V)
0	0.000	0.010
15	0.125	0.012
25	0.214	0.012
50	0.448	0.014
75	0.710	0.013
85	0.822	0.012
100	1.000	0.006

Table 4: Standard Cell Potential for DGM-PC System

| % DGM	Mole fraction	E°_{cell} (V)
0	0.000	0.011
15	0.095	0.013
25	0.167	0.014
50	0.374	0.015
75	0.643	0.015
85	0.772	0.013
100	1.000	0.007

The rate at which reactions occur in the half-cells depend on a number of factors which include the number of solvent ligands bound to the Mg^{2+}. The values of E°_{cell} were higher for DGM-PC than DME-PC, suggesting better coordination with the three oxygen atoms of DGM molecules. This coordination by DGM afforded better complex stability for Mg^{2+} and consequently influenced the reaction rate with the result that E°_{cell} values were higher in DGM-PC system than in DME-PC system.
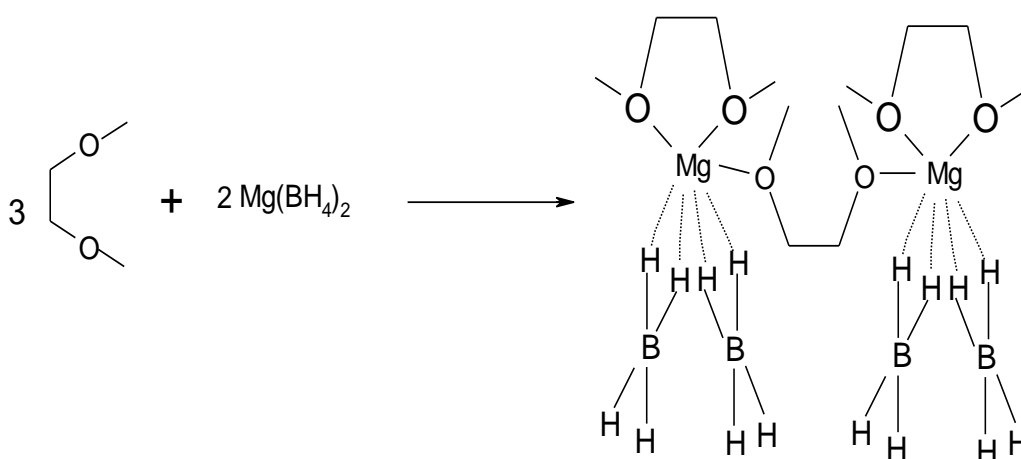
Solvated structures

The interaction between Mg^{2+} and the ligand (DME / DGM / PC) can be considered as a Lewis acid-base reaction. The Mg^{2+} acted as a Lewis acid by accepting and sharing pairs of electrons from the oxygen atoms (Lewis base) to form the metal-ligand coordinate covalent bonds (Chang and Goldsby, 2013). DGM is a tridentate chelating ligand and has three lone pairs of electrons on the oxygen for donation and sharing with Mg^{2+} to yield the solvation of the cation. The solvent composition 100% DGM by volume, only a single DGM molecule orients about the

Mg^{2+} to form the most stable complex (Figure 1). DME is a bidentate chelating ligand with two lone pairs of electrons on the oxygen atom for donation and sharing with Mg^{2+} which will lead to the solvation of $Mg(BH_4)_2$ salt. At the solvent composition of 100% DME (vol.%), three molecules of DME orient about the two moles of $Mg(BH_4)_2$ to form the less stable complex (Figure 2). PC is a non-chelating ligand and by nature is monodentate. At the solvent composition of 100% PC (vol.%), three molecules of PC orient about one mole of $Mg(BH_4)_2$ salt and primarily solvated the magnesium ions. The complex formed with PC is the least stable (Figure 3).
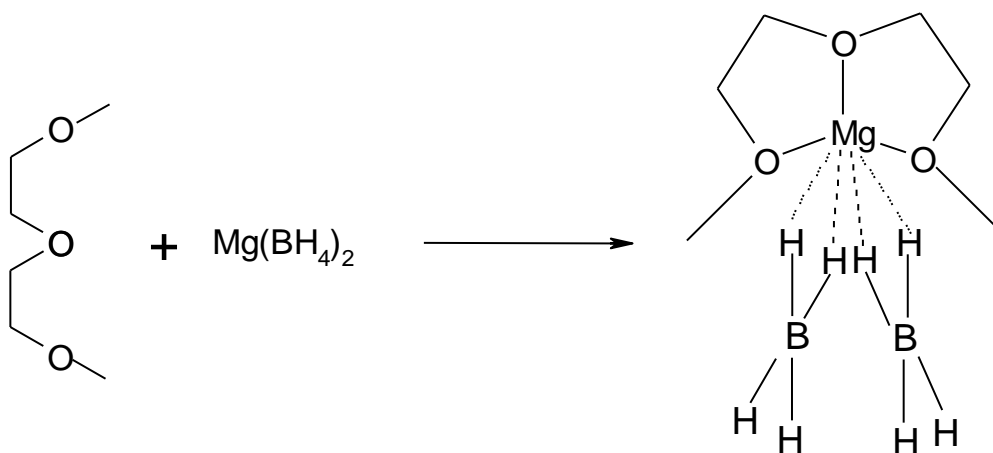
Figure 1: Solvated structure of $Mg(BH_4)_2$ in 100% DGM by volume

Figure 2: Solvated structure of $Mg(BH_4)_2$ in 100% DME by volume
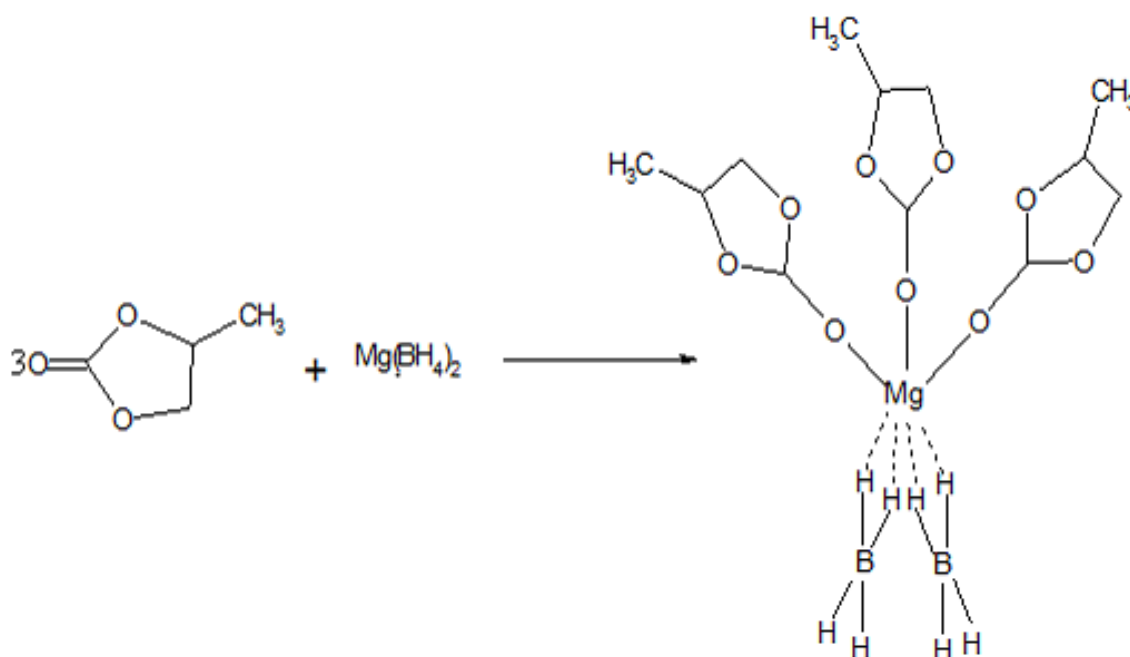
Figure 3: Solvated structure of Mg(BH$_4$)$_2$ in 100% PC by volume

CONCLUSION

The study on the cell potential of electrolyte solution provides valuable insight into the thermodynamic properties of systems. The improved reaction rates account for the increase in the measured cell potential in both systems studied over the constitution range of 0 – 50 % vol. of DME or DGM. A progressive drop in cell potential values was observed over the composition range 50 – 100 % of DME or DGM, signifying chemical reaction of lesser rate. The negative values of Gibbs free energy change over the entire composition range for DME-PC and DGM-PC systems attest to the spontaneity of the reactions in the concentration cells. The results from the study confirm that the electrolyte constituted with DGM-PC is more favorable in terms of thermodynamics, as Mg coordination complexes appear to be more stable in this medium. The formation of stable Mg complex is critical for the efficiency of battery functionality and durable performance of the electrochemical system.

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